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"VAPOR-LIQUID EQUILIBRIA IN PHENOL-HYDROCARBON SYSTEMS"

SECTION II

"APPLICATION OF EXPERIMENTAL VAPOR-LIQUID EQUILIBRIA TO AN ANALYSIS OF THE OPERATION OF A COMMERCIAL UNIT FOR THE PURIFICATION OF TOLUENE FROM PETROLEUM"

by

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SECTION I

VAPOR-LIQUID EQUILIBRIA IN PHENOL-HYDROCARBON SYSTEMS

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Abstract

Vapor-liquid equilibria at atmospheric pressure have been obtained on systems encountered in the purification of toluene from petroleum, including mixtures of toluene, methylcyclohexane, paraffin hydrocarbons, and phenol. These data have been correlated on the basis of relationships previously proposed.

Introduction

The necessity for designing fractional distillation and absorption equipment for non-ideal systems has stimulated interest in the vapor-liquid equilibrium relationships in these systems, which include solutions under high pressure, solutions of hydrocarbons having widely different boiling points such as methane and crude oil, and solutions of hydrocarbons having different structures, such as paraffins, naphthenes, and aromatics, as well as many solutions of hydrocarbons and non-hydrocarbons. This paper presents vapor-liquid equilibrium data for several non-ideal systems, both hydrocarbon and hydrocarbon-nonhydrocarbon, and a brief theoretical treatment of non-ideal solutions with the object of estimating such equilibrium relationships from incomplete data.

Experimental Work

In the commercial production of toluene from petroleum, the toluene, boiling at 231° F., must be separated from paraffinic and naphthenic hydrocarbons, having about the same boiling point and volatility. Thus, the separation of toluene as a pure compound by ordinary fractionation is very difficult. In the presence of phenol, however, toluene may be separated with ease, since the volatilities of the paraffins and naphthenes relative to that of toluene are considerably increased. In order to determine the equilibrium relationships involved in this operation, vapor-liquid equilibrium data were obtained on the following systems at atmospheric pressure.

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Binary Systems

1. Isooctane (2,2,4 trimethylpentane)-toluene
2. Toluene-phenol
3. Methylcyclohexane-phenol
4. Isooctane-phenol
5. Isononane-phenol

Ternary Systems

1. Methylcyclohexane-toluene-phenol
2. Isooctane-toluene-phenol
3. Isononane (2,2,5 trimethylhexane)-toluene-phenol
4. Methylcyclohexane-toluene-sludge
5. Isooctane-toluene-sludge

Quaternary

1. Isooctane-methylcyclohexane-toluene-phenol

Data are available in the literature on the systems methylcyclohexane-toluene,[11] toluene-*n*-heptane,[1] toluene-*n*-octane,[1] benzene-*n*-hexane,[13] benzene-cyclohexane,[12] and benzene-methylcyclopentane.[5] Unpublished data were available on the system paraffin cut (230° F. boiling point)-phenol. All of these data were used in the correlations presented in this investigation.

Materials Used

Table I gives the more important physical properties of the materials used as compared with the corresponding properties of the pure substances.

The toluene was produced at Pan American Refining Corp. and was 99.5% pure. It was caustic washed to remove traces of phenol.

The methylcyclohexane was obtained from the Curtin Chemical Company of Houston, Texas. It contained about 3% aromatics and had a refractive index of 1.4230 at 25° C. It was thoroughly shaken for five minutes with 98% sulphuric acid using a 1 to 1 volumetric ratio. This process was repeated, then the methylcyclohexane was water washed, caustic washed, water washed, and dried with calcium sulphate.

The isooctane (2,2,4 trimethylpentane) was fractionated from a 100 octane reference fuel in a half inch diameter column packed with glass helices equivalent to 30 theoretical plates operated at a reflux ratio of 10 to 1.

The isononane (2,2,5 trimethylhexane) was fractionated from amylene alkylate. A cut having a 10° boiling range was fractionated from the alkylate on a high capacity column. This cut was refractionated on the above 30 plate column at a reflux ratio of 10 to 1.

TABLE I.—PHYSICAL CONSTANTS OF COMPOUNDS USED IN EXPERIMENTAL WORK

Compound	Boiling Point, °F.		Refractive Index N_D^{25}		Specific Gravity at 25° C.	
	Standard	Measured	Standard	Measured	Standard	Measured
Toluene	231.1[3]	231.0—231.4	1.4940[2]	1.4936	.863[2]	.862
Methylcyclohexane	213.7[2]	213.4—213.8	1.4206[2]	1.4207	.765[2]	.765
2,2,4 Trimethylpentane	210.6[2]	210.0—211.0	1.3890[2]	1.3890	.689[2]	.689
2,2,5 Trimethylhexane	255.4[3]	254.6—256.2	1.3973[3]	1.3976	.7036[3]	.704
Phenol	360.2[7]	360	1.5442[7]	1.5420	1.071[7]	1.071
Sludge	——	484	———	1.52	——	1.025

The phenol was commercial phenol obtained from the Monsanto Chemical Company. It was completely caustic soluble and contained 98.5-99% phenol, the impurities being largely cresols.

Equipment Used

The equilibrium still used for most of the work was essentially similar to the one described by Othmer.[10] Another equilibrium still similar to the one described by Jones, Schoenborn and Colburn,[4] was also used for part of the work.

The results obtained on the two stills check within the experimental accuracy of each unit. The chief advantages of the Jones still are; the ease of construction and a greater variety of sizes so that when only a limited amount of material is available more points can be obtained; and the location of the thermowell at the point of contact of the liquid and the vapor phases, rather than in the vapor phase, eliminated the possibility of small errors in temperature due to slight superheating of the vapor.

Experimental Results

Binary Systems. The experimental data for the systems isooctane-phenol, phenol-toluene, phenol-methylcyclohexane, and phenol-isooctane are presented in Tables II, III, IV, and V. The phenol-isooctane data are not reliable above 10% phenol in the liquid phase, because of the limited solubility of phenol in paraffin hydrocarbons. Similarly the methylcyclohexane-phenol data are unreliable above 30% phenol in the liquid phase.

In addition, three determinations were obtained at low phenol concentrations in the system isononane-phenol. These data are shown in Table VI.

Ternary Systems. Vapor-liquid equilibria were obtained on the ternary systems methylcyclohexane-toluene-phenol and isooctane-toluene-phenol over the entire range of phenol and hydrocarbon concentrations. The experimental data are presented in Tables VII and VIII. The smoothed bubble point temperatures are shown as a function of composition in Figures 1 and 2.

Twenty-eight runs were made in the system isononane-toluene-phenol at phenol concentrations above 40% in the liquid phase, in order to study the effect of paraffin boiling point on the equilibria in systems consisting of phenol, toluene, and paraffin hydrocarbons. These data are shown in Table IX and Figure 3.

Four vapor-liquid equilibrium determinations were made in the systems sludge-toluene-methylcyclohexane and sludge-toluene-isooctane. This sludge is a reaction product of diolefins and phenol formed in commercial units. These data are listed in Table X.

Quaternary Systems. Eighteen points were obtained in the system toluene-methylcyclohexane-isooctane-phenol to investigate the application of ternary data to quaternary systems. These data are presented in Table XI. Twelve of these points were obtained at high phenol concentrations (above 40 mole % in the liquid). The remaining six points were obtained at phenol concentrations of 20% or less in the liquid.

TABLE II.—VAPOR-LIQUID EQUILIBRIA

System Toluene-Isooctane

Pressure—760 mm. Hg.

Run No. *TP*	Equilibrium Temp., ° F.	Vapor Mole % Toluene	Liquid Mole % Toluene	Activity Coefficients	
				Isooctane	Toluene
16	230.5	96.55	97.98	1.262	1.00
15	228.4	88.75	93.01	1.238	1.005
1	228.2	87.62	92.64	1.266	0.981
14	225.2	79.70	86.00	1.18	1.012
13	225.0	69.80	78.20	1.14	1.02
3	225.2	61.94	71.36	1.090	0.982
12	219.0	49.50	59.03	1.057	1.04
5	218.0	45.10	52.88	1.008	1.028
11	217.6	40.40	47.96	1.048	1.05
2	217.0	36.08	42.07	0.983	1.058
7	215.0	32.54	38.20	1.010	1.089
4	214.0	23.27	27.80	1.000	1.094
10	212.3	17.10	19.80	1.01	1.158
6	212.0	9.90	11.30	0.982	1.170
8	211.2	7.40	8.19	0.990	1.240
9	211.0	3.15	3.39	1.005	1.26

TABLE III.—VAPOR-LIQUID EQUILIBRIA

System Toluene-Phenol

Pressure 760 mm. Hg.

Run No. *AN*	Equilibrium Temp., ° F.	Vapor Mole % Phenol	Liquid Mole % Phenol	Activity Coefficients	
				Toluene	Phenol
13	343	65.90	95.65	1.700	.920
1	319	48.80	91.28	1.920	1.248
21	309	37.90	88.14	1.76	1.02
14	301	37.50	87.52	1.810	1.165
20	288	21.50	78.10	1.505	1.10
3	273	19.30	72.50	1.570	1.250
5	263	12.75	59.20	1.310	1.220
7	260	10.99	52.00	1.190	1.290
19	252	8.41	41.02	1.12	1.501
9	248.5	7.20	36.52	1.104	1.535
2	248	7.40	34.88	1.075	1.650
4	247.5	5.37	26.00	1.065	1.780
11	247	4.64	22.70	0.960	1.590
18	240	4.55	19.88	1.02	2.00
6	235	2.50	11.60	1.035	2.230
17	234	2.04	8.92	1.00	2.41
8	236	1.39	6.06	0.960	2.385
10	232	0.52	2.30	0.983	2.560
12	232	0.20	0.90	0.970	2.570
15	231	0.14	0.61	1.010	2.290
16	231	0.07	0.27	1.000	2.900

TABLE IV.—VAPOR-LIQUID EQUILIBRIA

System Methylcyclohexane-Phenol

Pressure 760 mm. Hg.

Run No. *M-F*	Equilibrium Temp., ° F.	Vapor Mole % Phenol	Liquid Mole % Phenol	Activity Coefficients	
				Methylcyclohexane	Phenol
9	302	32.25	88.60	1.630	1.02
8	266	12.90	73.80	1.560	1.04
1	248	11.60	62.00	1.290	1.41
3	234	9.12	34.80	1.000	2.76
2	222	6.16	9.74	0.895	8.80
4	216.5	3.17	4.82	0.960	10.75
5	216	2.59	3.89	0.970	11.14
6	215	0.86	1.26	0.972	12.13
7	214	0.37	0.48	0.980	14.16

TABLE V.—VAPOR-LIQUID EQUILIBRIUM DATA

System Isooctane-Phenol

Pressure 760 mm. Hg.

Run No. *AP*	Equilibrium Temp., ° F.	Vapor Mole % Phenol	Liquid Mole % Phenol	Activity Coefficients	
				Isooctane	Phenol
9	258	11.20	76.20	1.83	.915
8	236	6.36	57.30	1.46	1.130
7	226	8.60	33.40	0.82	2.200
1	219	5.41	9.85	1.01	9.000
2	214	3.07	4.70	1.00	11.200
3	214	2.96	4.54	1.00	11.150
4	213	1.36	2.05	1.00	11.500
5	213	0.86	1.08	1.00	13.800
66	212	0.34	0.41	1.00	14.400

TABLE VI.—VAPOR-LIQUID EQUILIBRIA

System Isononane-Phenol

Pressure 760 mm. Hg.

Run No. *AN*	Equilibrium Temp., ° F.	Vapor Mole % Phenol	Liquid Mole % Phenol	Activity Coefficients	
				Phenol	Isononane
1	259	3.41	3.52	6.01	1.00
2	256	0.64	0.64	6.62	0.99
3	256	0.29	0.29	6.62	0.99

Table VII.—Vapor-Liquid Equilibria

System Methylcyclohexane-Toluene-Phenol

Pressure 760 mm. Hg.

Run No. *AB*	Temp. ° F.	Vapor			Liquid			Activity Coefficients		
		Mole % Phenol	Mole % Toluene	Mole % Methyl-cyclo-hexane	Mole % Phenol	Mole % Toluene	Mole % Methyl-cyclo-hexane	Phenol	Toluene	Methyl-cyclo-hexane
1	260	13.88	76.60	9.52	63.82	34.32	1.86	1.33	1.408	2.48
2	258	12.40	70.30	16.70	63.84	32.80	3.36	1.23	1.38	2.47
3	256	11.60	65.30	23.10	64.05	31.35	4.60	1.21	1.38	2.58
4	252	11.60	58.50	29.90	65.00	28.65	6.35	1.31	1.40	2.56
5	250	9.60	55.35	35.05	64.90	27.63	7.47	1.12	1.386	2.53
11	250	8.94	82.10	8.96	52.85	44.89	2.26	1.17	1.265	2.12
12	245	7.31	68.67	24.02	53.34	40.12	6.54	1.145	1.28	2.12
13	242	7.21	57.27	35.53	53.00	36.55	10.45	1.145	1.24	2.03
21	276	17.50	73.10	9.40	74.40	24.30	1.30	1.05	1.56	2.92
22	274	17.30	59.70	23.00	72.95	23.40	3.65	1.08	1.34	2.56
23	264	14.58	52.82	32.60	72.90	21.63	5.47	1.10	1.404	2.68
24	259	15.22	23.19	61.59	74.91	12.00	13.09	1.14	1.26	2.315
25	252	10.89	37.81	51.30	69.69	19.41	10.90	1.10	1.44	2.59
26	249	10.60	11.20	78.20	73.70	6.59	19.71	1.06	1.26	2.26
31	295	21.80	69.50	8.70	82.01	17.11	.88	.80	1.575	3.05
32	287	22.70	56.90	20.40	81.53	16.14	2.38	.98	1.58	3.09
33	280	21.40	47.23	31.37	79.94	15.95	4.11	1.09	1.44	2.86
34	296	28.98	17.01	54.01	87.50	5.51	6.99	.98	1.41	2.76
35	281	23.40	10.32	60.28	83.39	4.50	12.11	.93	1.19	2.22
36	274	20.20	19.79	60.01	80.22	8.69	11.09	.98	1.35	2.45
41	241	5.80	68.30	25.90	41.20	49.50	9.30	1.30	1.16	1.79
42	239	5.20	60.80	34.00	43.20	43.80	13.00	1.14	1.08	1.64
43	240	5.76	80.18	14.06	41.01	54.19	4.80	1.36	1.03	1.61
51	239	6.30	70.00	23.70	37.25	54.49	8.26	1.56	1.13	1.77

TABLE VII.—(*Continued*)

Run No. *AB*	Temp. ° F.	Vapor			Liquid			Activity Coefficients		
		Mole % Phenol	Mole % Toluene	Mole % Methyl-cyclo-hexane	Mole % Phenol	Mole % Toluene	Mole % Methyl-cyclo-hexane	Phenol	Toluene	Methyl-cyclo-hexane
52	237	4.85	47.00	48.15	34.59	42.81	22.60	1.36	1.00	1.44
53	237	4.64	43.70	51.66	34.78	39.62	25.60	1.30	1.00	1.36
54	232	4.49	23.50	72.01	26.70	25.10	48.20	1.81	.94	1.12
55	230	4.42	16.40	79.18	25.96	17.97	56.07	1.88	.98	1.10
56	234	4.61	20.85	74.54	34.15	21.25	44.60	1.46	.935	1.208
57	230	3.74	9.88	86.38	32.19	10.69	57.12	1.29	.953	1.10
61	236	4.87	74.00	21.13	22.32	67.07	10.61	2.2	1.01	1.395
62	231	3.52	53.25	43.23	19.33	54.90	25.77	1.98	.99	1.3
63	234	4.24	40.60	55.16	28.64	40.56	30.80	1.57	.99	1.32
64	230	3.76	28.23	68.01	24.45	30.42	45.13	1.712	.975	1.2
65	228	3.67	21.30	75.03	20.56	23.45	55.99	2.03	.98	1.091
71	230	2.10	72.15	25.75	10.35	73.83	15.82	2.39	.98	1.245
72	226	1.49	55.06	41.45	7.21	62.23	30.56	2.59	.98	1.108
73	223	1.56	38.30	60.14	5.71	44.44	49.85	3.75	1.00	1.05
74	218	1.54	26.06	72.40	3.66	28.40	67.94	6.20	1.086	.949
81	226.5	1.37	63.81	34.82	5.28	70.32	24.40	3.21	.98	1.14
82	224	2.09	30.61	67.30	8.84	34.66	56.50	2.94	.94	.97
91	228	2.12	60.25	31.63	9.81	64.39	25.80	2.58	.97	1.08
92	224	1.81	33.55	64.64	7.41	38.25	54.34	3.26	.99	1.02
101	257	8.60	37.30	54.10	69.50	18.52	11.98	.92	1.35	2.365
102	243	5.28	11.37	83.35	61.30	8.12	30.58	.75	1.15	1.725
103	247	7.13	25.90	66.97	63.27	16.36	20.37	.91	1.21	1.91
104	255	8.43	27.85	63.72	69.28	14.90	15.82	.82	1.28	2.13
105	247	6.66	16.01	77.33	65.98	10.08	23.94	.80	1.25	1.92
106	251	7.18	11.47	81.35	69.64	6.71	23.65	.75	1.24	1.89
107	246	6.11	6.80	87.09	63.58	4.69	31.73	.78	1.15	1.655
121	286	20.67	26.70	52.63	86.40	7.65	5.95	.83	1.505	2.96

TABLE VII.—(*Continued*)

Run No. *AB*	Temp. ° F.	Vapor			Liquid			Activity Coefficients		
		Mole % Phenol	Mole % Toluene	Mole % Methyl-cyclo-hexane	Mole % Phenol	Mole % Toluene	Mole % Methyl-cyclo-hexane	Phenol	Toluene	Methyl-cyclo-hexane
122	284	18.78	19.90	61.32	85.41	6.41	8.18	.82	1.422	2.69
111	259	11.60	32.20	56.20	72.53	15.74	11.73	.98	1.345	2.42
112	255	9.80	21.70	68.50	71.40	11.72	16.88	.91	1.28	2.16
113	251	6.74	10.73	82.53	70.51	6.22	23.27	.74	1.265	2.00
114	262	11.10	16.55	72.35	78.30	7.49	14.21	.83	1.38	2.45
115	258	9.45	11.29	79.26	75.84	5.60	18.56	.77	1.325	2.24
116	256	8.00	7.09	84.91	76.25	3.56	20.19	.72	1.36	2.23
123	280	15.40	10.20	74.40	85.07	3.40	11.53	.73	1.45	2.45
124	282	19.45	34.10	46.45	82.55	11.21	6.24	.95	1.45	2.77
124	276	16.19	25.30	58.51	81.83	9.22	8.95	.88	1.39	2.64
131	240	5.45	42.80	51.75	49.51	31.98	18.51	1.03	1.12	1.80
132	239	4.63	22.00	73.37	50.52	17.65	31.83	.88	1.092	1.53
133	238	4.11	11.40	84.49	50.12	9.85	40.03	.85	1.04	1.42
134	243	6.50	31.41	62.89	56.18	22.40	21.42	1.00	1.16	1.84
135	240	5.04	19.16	75.80	54.10	15.72	30.18	.87	1.05	1.665
136	239	4.57	8.02	87.41	52.48	6.58	40.94	.82	1.055	1.415
141	248	7.45	59.57	32.98	43.95	44.20	12.21	1.30	1.03	1.59
142	237	5.00	38.69	56.31	40.68	33.78	25.54	1.20	1.005	1.50
143	245	4.70	25.50	69.80	37.94	24.80	37.26	1.26	.99	1.38
144	238	5.15	13.33	81.52	46.00	12.18	41.82	1.04	.98	1.31
145	236	5.73	17.45	76.75	42.60	16.80	40.60	1.39	.94	1.336
146	235	4.76	8.49	86.75	42.05	7.50	50.45	1.17	.99	1.235
151	322	45.68	40.20	14.12	93.98	5.42	6.40	.90	2.09	4.83
152	302	26.48	35.80	37.88	89.90	7.23	2.87	.79	1.78	3.73
161	282	20.25	56.30	27.45	79.18	17.81	3.01	1.01	1.49	2.87
162	268	11.29	9.41	79.40	81.12	4.09	14.79	.83	1.45	2.60
171	260	12.69	66.31	21.00	64.81	31.02	4.17	1.18	1.36	2.50

TABLE VIII.—VAPOR-LIQUID EQUILIBRIA

System Isooctane-Toluene-Phenol

Pressure 760 mm. Hg.

Run No. *AB*	Temp. ° F.	Vapor			Liquid			Activity Coefficients		
		Mole % Phenol	Mole % Toluene	Mole % Isooctane	Mole % Phenol	Mole % Toluene	Mole % Isooctane	Phenol	Toluene	Isooctane
1	268	15.98	74.43	9.59	67.37	31.50	1.13	1.1	1.376	3.73
2	262	12.22	66.58	21.20	62.00	34.43	3.57	1.17	1.23	2.94
3	260	11.05	53.16	35.99	67.67	26.65	5.68	1.04	1.28	3.035
4	251	8.92	29.40	61.68	72.44	16.54	11.02	.9	1.3	3.10
5	230	5.13	3.89	90.98	71.45	3.14	25.41	.82	1.24	2.62
6	230	6.54	14.05	79.41	72.63	9.56	17.81	.88	1.34	2.98
7	234	5.68	10.82	83.50	70.10	7.90	22.00	.85	1.29	2.66
8	231	6.68	10.38	82.59	63.60	8.90	27.50	.96	1.16	2.2
21	225	4.43	3.90	91.67	48.90	4.03	47.07	1.21	1.05	1.55
22	240	7.08	41.14	51.78	53.96	31.95	14.09	1.2	1.12	2.33
23	234	5.14	29.42	65.44	50.60	26.10	23.30	1.11	1.11	1.98
24	231	4.69	15.88	79.43	54.80	14.78	30.42	1.04	1.082	1.925
31	272	16.54	55.78	27.68	74.70	22.18	3.12	1.05	1.38	3.65
32	264	13.60	39.09	47.31	77.30	16.80	5.90	.77	1.41	3.78
33	251	9.50	22.70	67.80	76.59	12.20	11.21	.90	1.367	3.31
34	235	6.22	12.00	82.78	69.86	8.96	21.18	.90	1.25	2.70
41	280	21.20	52.74	26.06	82.51	15.49	2.00	1.02	1.61	4.80
42	280	22.16	32.04	45.80	81.80	9.55	3.65	.98	1.635	4.65
43	257	11.25	23.58	65.17	82.41	9.89	7.70	.91	1.58	4.40
44	236	6.56	10.05	83.49	75.58	6.62	17.80	.85	1.38	3.16
51	242	6.40	61.00	32.60	41.36	48.34	10.30	1.80	1.072	1.93
52	236	5.97	40.10	53.93	40.83	37.23	21.94	1.47	1.00	1.64
53	234	5.60	32.92	61.48	40.76	31.81	27.43	1.42	.97	1.524
54	231	5.52	18.77	75.71	41.90	18.91	39.19	1.49	.985	1.401

TABLE VIII.—(*Continued*)

Run No. *AA*	Temp. °F.	Vapor			Liquid			Activity Coefficients		
		Mole % Phenol	Mole % Toluene	Mole % Isooctane	Mole % Phenol	Mole % Toluene	Mole % Isooctane	Phenol	Toluene	Isooctane
55	225	4.62	7.80	87.58	40.30	8.25	51.45	1.48	1.03	1.35
61	240	5.62	67.30	27.08	30.90	58.90	10.20	1.63	.97	1.64
62	234	5.44	48.75	45.81	28.60	49.60	21.80	1.98	.955	1.472
63	231	5.38	40.70	54.32	29.14	41.38	29.48	2.08	.98	1.335
64	226	5.44	22.35	72.21	26.93	24.57	48.50	2.58	.985	1.16
65	223	4.24	10.39	84.37	29.50	11.70	58.80	2.01	1.02	1.22
71	233	3.97	63.00	33.03	19.80	64.10	16.10	2.16	.96	1.45
72	230	4.54	52.10	44.16	20.80	55.40	23.80	2.46	.98	1.36
73	226	44.38	39.87	55.75	19.88	43.43	36.69	2.82	.98	1.195
74	222	4.11	24.59	71.30	19.89	28.09	52.02	3.05	1.009	1.13
75	220	4.69	9.85	85.41	20.35	11.16	68.49	3.35	1.035	1.065
81	229	2.10	68.44	29.56	9.94	73.48	16.58	2.5	.98	1.32
82	226	2.64	56.40	40.96	11.48	62.10	26.42	2.81	.98	1.21
83	222	2.54	41.15	56.31	9.00	48.50	42.50	3.99	.99	1.09
84	220	2.88	28.60	68.52	9.40	33.25	57.35	4.55	1.035	1.04
85	216	3.26	14.68	82.06	9.63	16.77	73.60	5.29	1.108	1.027
86	215	4.16	7.50	88.34	9.80	8.54	81.66	6.80	1.11	1.00
87	231	2.17	83.15	14.58	10.36	82.58	7.06	2.48	1.00	1.54
91	220	1.96	42.71	55.33	6.18	49.85	43.97	4.44	1.01	1.04
92	223	.85	70.16	28.99	3.06	78.53	18.41	3.58	.975	1.25
101	223	.68	71.65	27.67	1.82	80.08	18.10	4.81	.98	1.21
103	228	1.00	46.70	52.30	2.20	53.50	44.30	6.68	1.03	1.02
121	250	7.70	52.88	39.42	55.90	35.10	9.00	1.12	1.19	2.6
122	241	7.16	44.44	48.40	55.00	32.21	12.79	1.17	1.175	2.41
123	240	6.45	36.85	56.70	58.92	26.73	14.35	1.06	1.19	2.55
124	239	6.43	29.20	64.37	60.30	22.14	17.56	1.02	1.16	2.40
131	300	37.20	41.50	21.30	91.23	7.82	.95	1.00	1.95	6.35
132	253	13.60	3.06	83.34	92.30	1.26	6.44	1.02	1.86	6.80

TABLE VIII.—(*Continued*)

Run No. *AA*	Temp. ° F.	Vapor			Liquid			Activity Coefficients		
		Mole % Phenol	Mole % Toluene	Mole % Isooctane	Mole % Phenol	Mole % Toluene	Mole % Isooctane	Phenol	Toluene	Isooctane
141	248	8.46	62.34	29.20	48.98	43.88	7.14	1.32	1.07	2.31
142	240	7.18	54.35	38.47	47.63	41.58	10.79	1.36	1.11	2.33
143	239	6.13	41.89	51.98	48.10	34.80	17.10	1.21	1.07	2.00
144	237	6.05	36.08	57.10	48.30	31.78	19.92	1.26	1.086	1.94
151	260	11.72	58.68	29.60	65.80	29.72	4.48	1.081	1.275	3.205
152	245	8.20	44.20	47.60	59.20	30.24	10.56	1.06	1.19	2.71
153	248	8.13	38.47	53.40	65.53	23.73	10.74	1.00	1.29	2.96
154	240	6.85	33.80	59.35	61.59	23.78	14.63	1.01	1.20	2.57
155	233	5.78	11.80	82.42	63.86	9.80	26.34	.945	1.14	2.21
156	236	5.96	18.00	76.04	61.21	14.92	23.87	.975	1.11	2.125
157	260	11.80	54.98	33.22	65.55	29.15	5.35	1.10	1.25	3.06
158	227	4.45	3.30	92.25	59.35	3.11	37.54	.90	1.11	1.87
161	265	12.50	54.00	33.50	71.68	24.14	4.18	.99	1.36	3.63
162	256	10.60	35.86	53.54	71.92	19.18	8.90	.98	1.30	3.055
163	252	9.10	26.20	64.70	74.90	14.31	10.79	.87	1.325	2.98
164	230	5.20	3.70	91.10	74.40	2.80	22.80	1.795	1.35	3.26
171	283	22.63	53.55	23.82	83.56	14.80	1.64	1.04	1.69	5.15
172	235	7.44	2.80	89.76	83.00	1.79	15.21	.85	1.47	4.04
181	271	16.96	56.44	26.60	74.51	22.57	2.92	1.01	1.38	3.77
182	264	12.35	46.00	41.65	72.24	21.80	5.96	.966	1.285	3.20
183	252	10.07	37.95	53.98	70.62	20.40	8.98	1.01	1.33	3.25
184	247	8.15	29.60	64.25	69.37	17.71	12.92	.935	1.295	2.85
191	278	15.20	52.00	32.80	79.62	17.38	3.00	.92	1.49	4.18
192	270	12.38	44.80	42.82	78.10	17.18	4.72	.86	1.43	3.84
193	260	10.17	35.40	54.43	76.39	15.97	7.69	.87	1.41	3.405
201	248	7.80	50.90	41.30	54.14	36.00	9.86	1.21	1.095	2.36
202	239	7.53	40.74	51.73	52.40	32.52	15.08	1.30	1.09	2.18
203	238	7.36	33.30	59.34	53.35	27.85	18.80	1.22	1.07	2.03

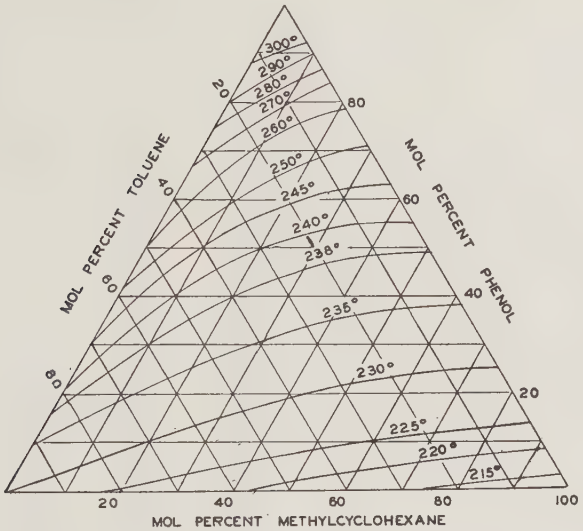

FIG. 1. Bubble Point Compositions, Atmospheric Pressure. System: Toluene-Methylcyclohexane-Phenol.

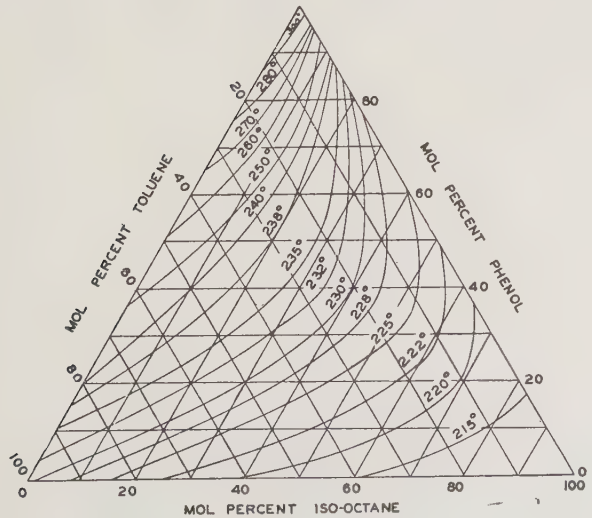

FIG. 2. Bubble Point Compositions, Atmospheric Pressure. System: Toluene-Isooctane-Phenol.

TABLE IX.—VAPOR-LIQUID EQUILIBRIA

System Isononane-Toluene-Phenol

Pressure 760 mm. Hg.

Run No. *AE*	Temp. ° F.	Vapor			Liquid		
		Mole % Phenol	Mole % Toluene	Mole % Iso-nonane	Mole % Phenol	Mole % Toluene	Mole % Iso-nonane
1	266	13.94	59.66	26.40	66.69	26.60	6.71
2	263	12.82	45.65	41.48	65.42	21.20	13.38
3	261	10.86	29.76	59.38	62.91	15.31	21.78
4	266	11.30	13.18	75.52	63.20	6.50	30.30
11	286	21.27	60.40	18.33	81.98	15.76	2.26
12	284	20.58	47.46	31.96	81.40	14.16	4.54
13	272	16.60	10.70	73.30	80.95	4.10	14.95
21	262	12.48	66.90	20.62	62.40	31.06	6.54
22	262	11.52	36.60	51.88	63.70	17.23	19.05
31	271	14.90	63.85	21.25	69.73	25.40	4.87
32	269	15.29	46.25	38.46	69.60	20.40	10.00
33	269	14.21	36.20	49.59	69.78	15.80	14.42
34	268.5	12.36	27.38	60.26	71.36	11.62	17.02
35	271	16.40	5.69	77.91	76.84	2.30	20.36
41	256.4	10.89	59.00	30.11	51.50	35.56	12.94
42	255	10.69	51.50	37.81	53.25	30.20	16.55
43	256	10.08	42.94	46.98	52.35	25.20	22.45
44	252	9.89	31.59	58.52	45.80	20.00	34.20
45	262	10.29	8.60	81.11	55.40	4.65	39.95
61	265.5	14.08	69.34	16.58	67.79	28.42	3.79
62	273	16.40	57.50	26.10	75.58	19.36	5.06
63	266	12.69	45.74	41.57	67.89	20.45	11.66
71	260	11.97	46.35	41.68	59.23	24.45	16.32
72	262	11.82	77.01	11.17	63.31	33.80	2.89
81	280	17.65	63.23	19.12	74.42	22.05	3.53
82	275	15.90	47.49	36.61	74.60	17.46	7.94

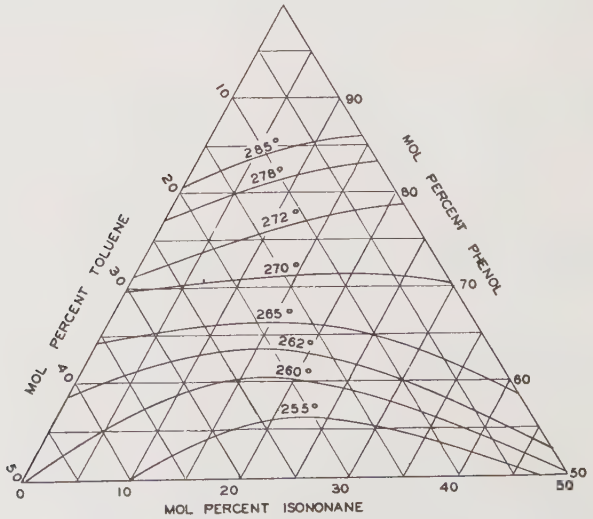

FIG. 3. Bubble Point Compositions, Atmospheric Pressure. System: Phenol-Isononane-Toluene.

TABLE X.—VAPOR-LIQUID EQUILIBRIA

Systems Containing Sludge

Pressure 760 mm. Hg.

Run No. *SM*	Equilibrium Temp. ° F.	Vapor			Liquid		
		Mole % Sludge	Mole % Toluene	Mole % Methylcyclohexane	Mole % Sludge	Mole % Toluene	Mole % Methylcyclohexane
1	268	1.09	71.88	27.03	61.47	30.82	7.71
2	248	1.36	36.96	61.88	52.12	21.06	26.82

Run No. *SP*	Equilibrium Temp. ° F.	Vapor			Liquid		
		Mole % Sludge	Mole % Toluene	Mole % Isooctane	Mole % Sludge	Mole % Toluene	Mole % Isooctane
1	268	0.90	77.40	21.60	63.50	31.25	5.34
2	281	2.00	67.52	30.48	71.05	22.30	6.15

DISCUSSION

Binary Systems

The experimental data for the binary systems were correlated by the procedure suggested by White [17] who presented the van Laar [14,15,16] equations for binary mixtures as follows:

$$T \log \gamma_1 = \left[\frac{\frac{a_{21}}{{b_1}^{1.5}}}{\frac{x_1}{x_2} + \frac{b_2}{b_1}} \right]^2 \qquad (1)$$

$$T \log \gamma_2 = \left[\frac{\frac{a_{12}}{{b_2}^{1.5}}}{\frac{x_2}{x_1} + \frac{b_1}{b_2}} \right]^2 \qquad (2)$$

where

$$a_{12} = -a_{21} = (b_2 \sqrt{a_1} - b_1 \sqrt{a_2})c \qquad (3)$$

In these equations, the signs of the $\frac{a_{21}}{b^{1.5}}$ constants are immaterial because the entire expression is squared. When $(T \log \gamma_1)^{-0.5}$ is plotted as a function of x_1/x_2 and $(T \log \gamma_2)^{-0.5}$ is plotted as a function of x_2/x_1, straight lines should result. The reciprocals of the slopes of the lines are equal to $\frac{a_{21}}{{b_1}^{1.5}}$ and $\frac{a_{12}}{{b_2}^{1.5}}$ respectively. The values of $\frac{b_2}{b_1}$ may be cal-

TABLE XI.—VAPOR-LIQUID EQUILIBRIA

System Toluene-Methylcyclohexane-Isooctane-Phenol

Pressure 760 mm. Hg.

Run No. *AC*	Temp. ° F.	Vapor				Liquid			
		Mole % Phenol	Mole % Toluene	Mole % Methyl-cyclo-hexane	Mole % Isooctane	Mole % Phenol	Mole % Toluene	Mole % Methyl-cyclo-hexane	Mole % Isooctane
51	255	10.21	49.32	8.31	32.16	68.03	25.35	1.83	4.79
52	257	9.54	49.37	28.00	19.09	69.07	23.40	5.57	1.96
53	245	7.77	33.40	46.00	12.83	58.50	23.19	15.25	3.06
54	243	8.15	26.40	24.85	40.60	65.68	17.56	7.84	8.92
61	244	7.75	46.18	35.49	10.58	49.02	35.10	12.88	3.00
62	242	6.28	42.42	14.20	37.10	49.58	34.81	5.13	10.48
63	240	7.40	21.15	52.63	18.82	46.88	18.88	26.27	7.97
64	230	6.55	18.44	31.33	43.68	43.75	18.23	17.66	20.36
71	241	7.10	52.20	11.25	29.45	46.16	41.20	4.16	8.54
72	233	5.68	15.02	48.95	30.35	50.36	13.70	23.85	12.09
73	230	5.49	15.15	11.61	67.75	54.85	14.00	5.59	25.56
74	235	6.37	26.20	28.45	38.98	51.40	22.40	12.70	13.50
81	221	2.62	36.06	48.16	13.16	10.71	41.08	38.68	9.53
82	220.5	2.46	37.60	9.77	50.17	9.79	43.12	7.13	39.96
83	216	3.89	11.48	74.94	9.69	12.68	12.51	67.09	7.72
84	215	5.15	9.73	6.82	78.30	11.81	10.49	5.55	72.15
91	223	3.10	30.70	58.35	7.85	18.51	33.41	43.12	4.96
92	225	4.00	31.57	6.07	58.36	20.63	34.40	3.95	41.02

culated from the relationship: intercept equals $\frac{b_2}{b_1} \times$ slope (or $\frac{b_1}{b_2} \times$ slope for component 2), or from the relationship: $\left(\frac{b_2}{b_1}\right)^{1.5}$ equals the quotient of the slopes. The results must be consistent, as is shown in Table XII.

TABLE XII.—CONSTANTS FOR EQUATIONS OF STATE EXPERIMENTAL BINARY SYSTEMS

	$\frac{a_{21}}{b_1^{3/2}}$	$\frac{b_2}{b_1}$	$\frac{a_{12}}{b_2^{3/2}}$	$\frac{b_1}{b_2}$
(1) Isooctane	−8.0	1.0 (1.0)* (1.0)†		
(2) Toluene			+8.0	1.0
(1) Methylcyclohexane ...	−7.8	1.09 (1.07)* (1.085)†		
(2) Toluene			+6.9	0.935
(1) Toluene	−14.4	0.84 (0.855)* (0.82)†		
(2) Phenol			+19.6	1.17
BINARY SYSTEMS CALCULATED FROM EXTRAPOLATED TERNARY DATA				
(1) Isooctane	−22.4	0.84		
(2) Phenol			+(28.9) †	(1.18)*
(1) Methylcyclohexane ...	−20.6	0.93		
(2) Phenol			+(23.5) †	(1.075)*

* Calculated from relationship $\frac{b_2}{b_1} = \frac{1}{b_1/b_2}$

† Calculated from relationship $\left(\frac{a_{21}}{b_1^{3/2}}\right)\left(\frac{b_2^{3/2}}{a_{21}}\right) = \left(\frac{b_2}{b_1}\right)^{3/2}$

The method described, in effect, averages the properties of the straight lines to give constants which are consistent thermodynamically according to the Gibbs-Duhem equation (4,8). The applicability of equations (1) and (2) to the systems involved is determined by comparing activity coefficients computed from the equations with the activity coefficients calculated from the experimental data.

Typical binary data of this investigation are shown in Figure 4. The constants for the systems toluene-isooctane, toluene-methylcyclohexane, and toluene-phenol, calculated from the straight line plots such as those in Figure 4, are listed in Table XII. Activity coefficients calculated from these constants by equations (1) and (2) agree with those calculated from the experimental data within the accuracy of the experimental measurements as shown in Figure 5.

The data for the systems methylcyclohexane-phenol, isooctane-phenol, and isononane-phenol are limited in the composition range covered, because of the limited solubility of phenol in paraffin hydrocarbons at temperatures somewhat below the boiling point and consequent difficulties in operating the equilibrium stills. These data are insufficient to determine the location of straight lines with any accuracy and therefore ternary data were extrapolated to amplify these binary data.

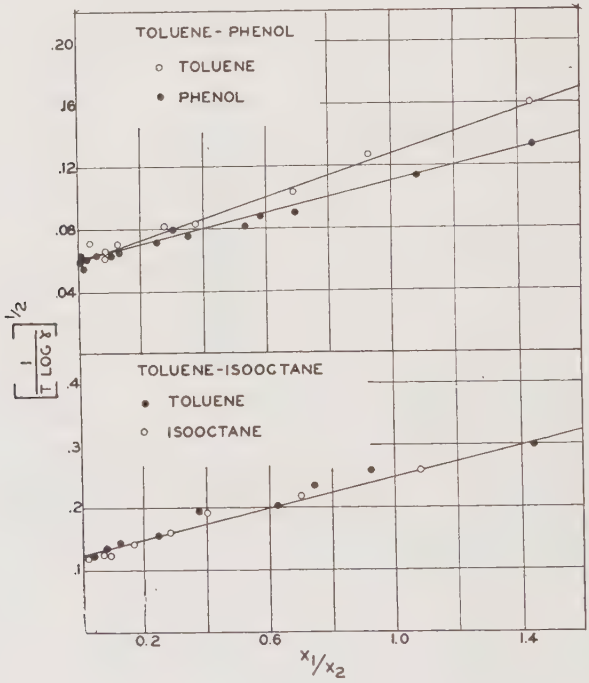

FIG. 4. Evaluation of Constants Binary Equation of State.

The activity coefficients calculated from the equilibrium data for ternary systems, toluene-isooctane-phenol and toluene-methylcyclohexane-phenol were plotted as a function of composition and smoothed by eye. The smoothed curves resulting are shown in Figures 7-14. The reliability of binary data extrapolated from ternary data was tested by extrapolating ternary data for toluene-isooctane-phenol and toluene-methylcyclohexane-phenol (Figures 7 and 10) to zero per cent isooctane and methylcyclohexane respectively. The comparison between the activity coefficients calculated for toluene from the binary data on the system toluene-phenol and the extrapolated activity coefficients as shown in Table XIII show excellent agreement, and justifies this procedure as a means of deriving binary data from ternary data where necessary.

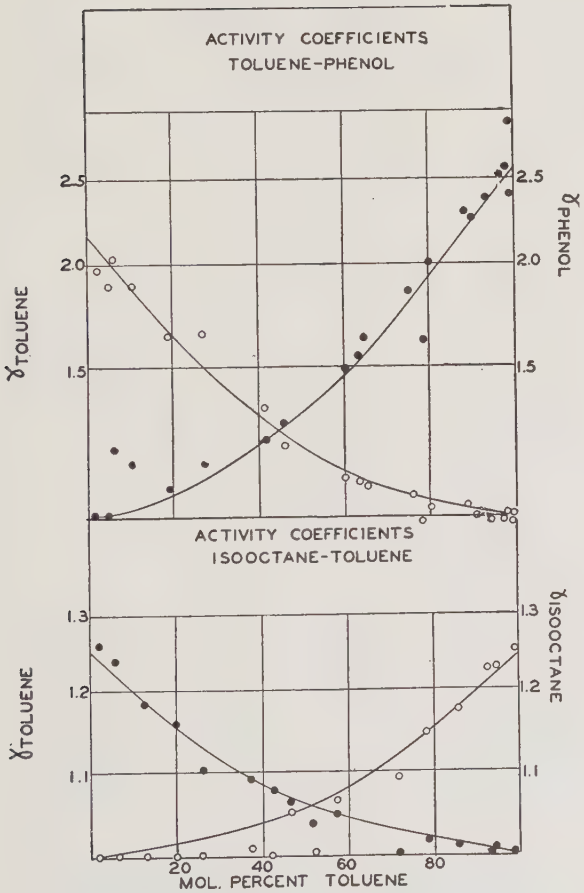
ACTIVITY COEFFICIENTS
TOLUENE-PHENOL
γTOLUENE
γPHENOL
2.5
2.0
1.5
ACTIVITY COEFFICIENTS
ISOOCTANE-TOLUENE
γTOLUENE
γISOOCTANE
1.3
1.2
1.1
20
40
60
80
MOL. PERCENT TOLUENE

FIG. 5.

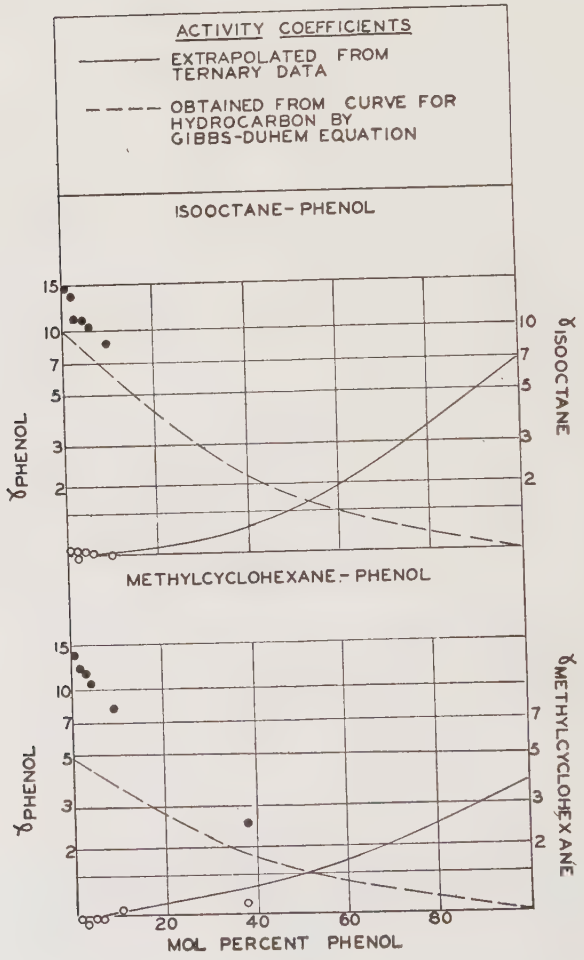
ACTIVITY COEFFICIENTS
EXTRAPOLATED FROM TERNARY DATA
OBTAINED FROM CURVE FOR HYDROCARBON BY GIBBS-DUHEM EQUATION
ISOOCTANE-PHENOL
METHYLCYCLOHEXANE-PHENOL
γ PHENOL
γ ISOOCTANE
γ METHYLCYCLOHEXANE
MOL PERCENT PHENOL
15
10
7
5
3
2
20
40
60
80

FIG. 6.

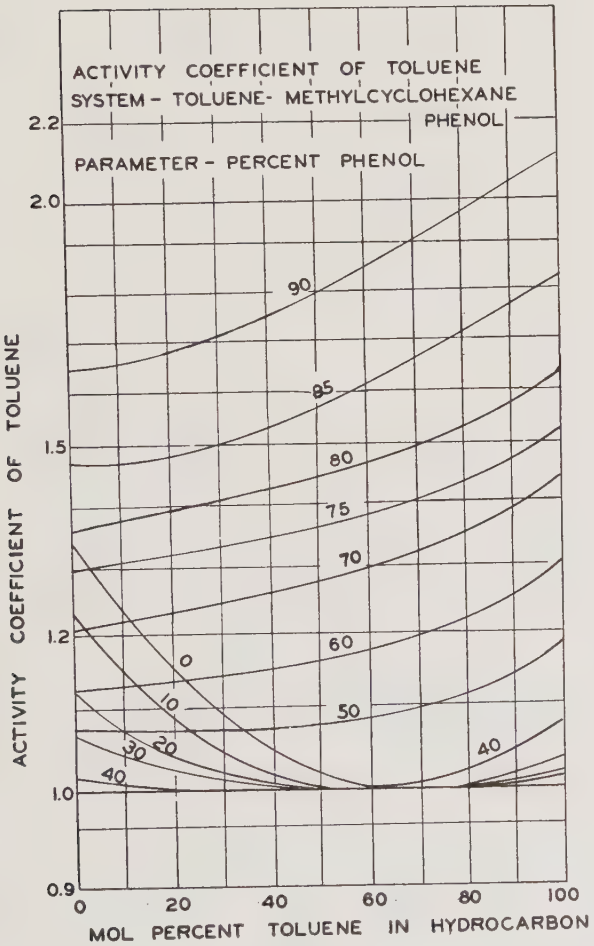
ACTIVITY COEFFICIENT OF TOLUENE
SYSTEM - TOLUENE- METHYLCYCLOHEXANE
PHENOL
PARAMETER - PERCENT PHENOL
ACTIVITY COEFFICIENT OF TOLUENE
MOL PERCENT TOLUENE IN HYDROCARBON
2.2
2.0
1.5
1.2
1.0
0.9
0
20
40
60
80
100
90
85
80
75
70
60
50
40
0
10
20
30
40

FIG. 7.

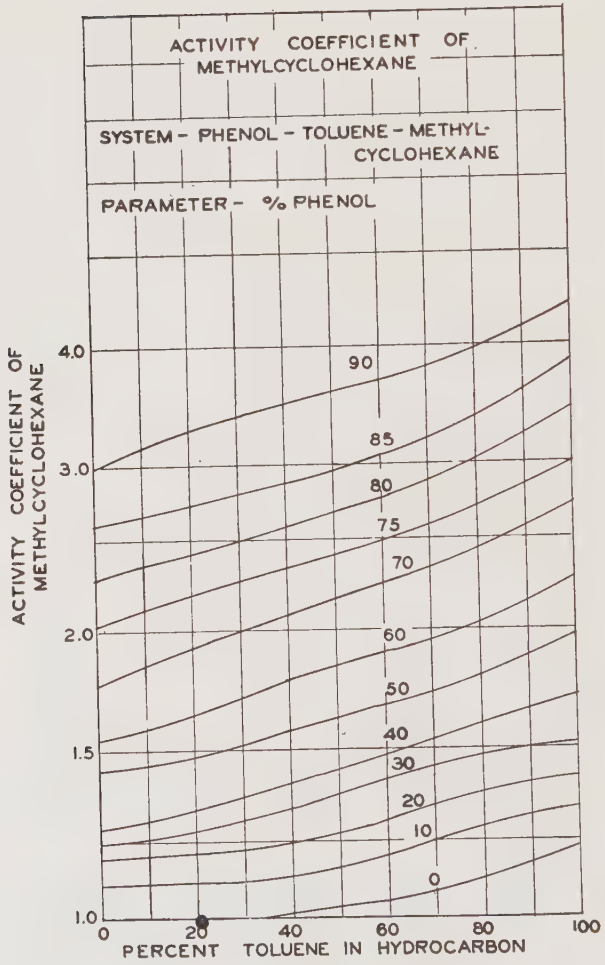
ACTIVITY COEFFICIENT OF METHYLCYCLOHEXANE
SYSTEM - PHENOL - TOLUENE - METHYL-CYCLOHEXANE
PARAMETER - % PHENOL
ACTIVITY COEFFICIENT OF METHYLCYCLOHEXANE
4.0
3.0
2.0
1.5
1.0
90
85
80
75
70
60
50
40
30
20
10
0
0
20
40
60
80
100
PERCENT TOLUENE IN HYDROCARBON

FIG. 8.

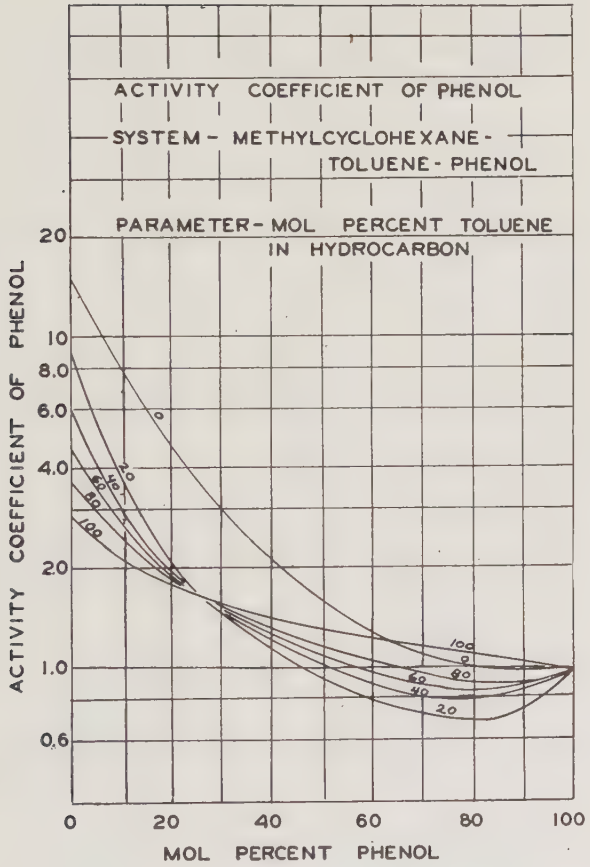
ACTIVITY COEFFICIENT OF PHENOL
SYSTEM - METHYLCYCLOHEXANE - TOLUENE - PHENOL
PARAMETER - MOL PERCENT TOLUENE IN HYDROCARBON
ACTIVITY COEFFICIENT OF PHENOL
MOL PERCENT PHENOL
20
10
8.0
6.0
4.0
2.0
1.0
0.6
0
20
40
60
80
100

FIG. 9.

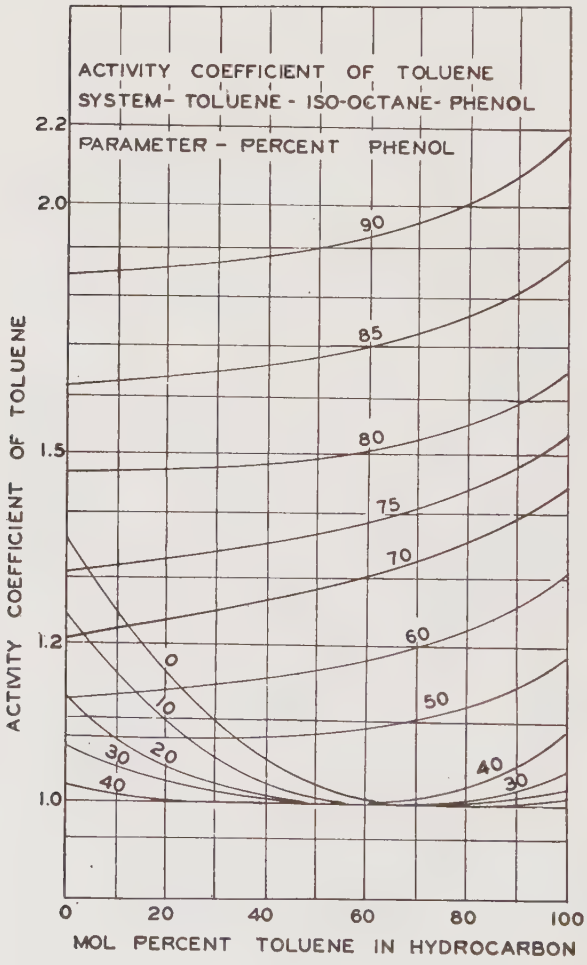
ACTIVITY COEFFICIENT OF TOLUENE
SYSTEM- TOLUENE - ISO-OCTANE- PHENOL
PARAMETER - PERCENT PHENOL
ACTIVITY COEFFICIENT OF TOLUENE
2.2
2.0
1.5
1.2
1.0
90
85
80
75
70
60
50
40
30
0
10
20
30
40
0
20
40
60
80
100
MOL PERCENT TOLUENE IN HYDROCARBON

FIG. 10.

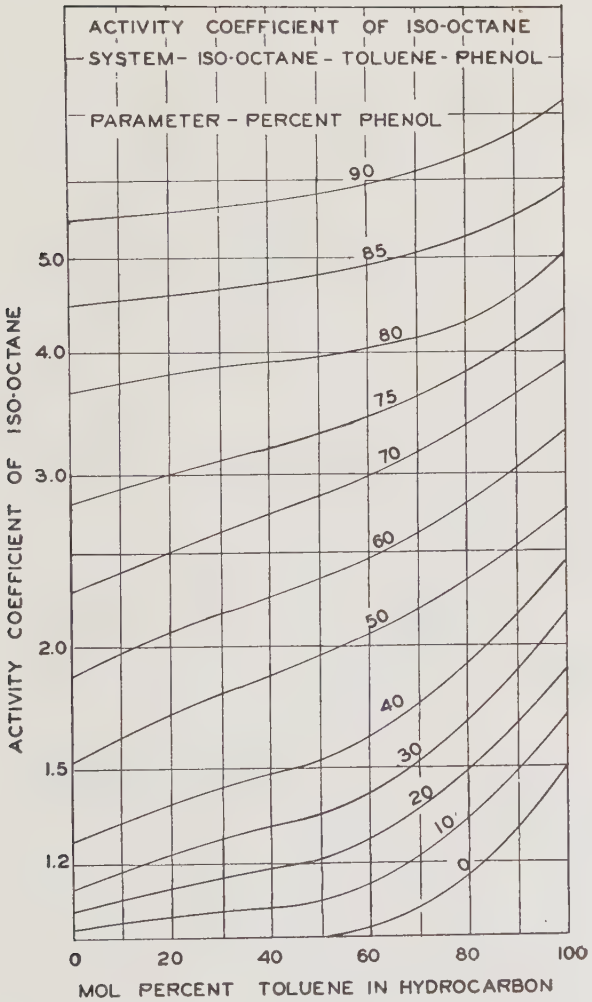
ACTIVITY COEFFICIENT OF ISO-OCTANE
SYSTEM- ISO-OCTANE - TOLUENE - PHENOL
PARAMETER - PERCENT PHENOL
90
85
80
75
70
60
50
40
30
20
10
0
ACTIVITY COEFFICIENT OF ISO-OCTANE
5.0
4.0
3.0
2.0
1.5
1.2
0
20
40
60
80
100
MOL PERCENT TOLUENE IN HYDROCARBON

FIG. 11.

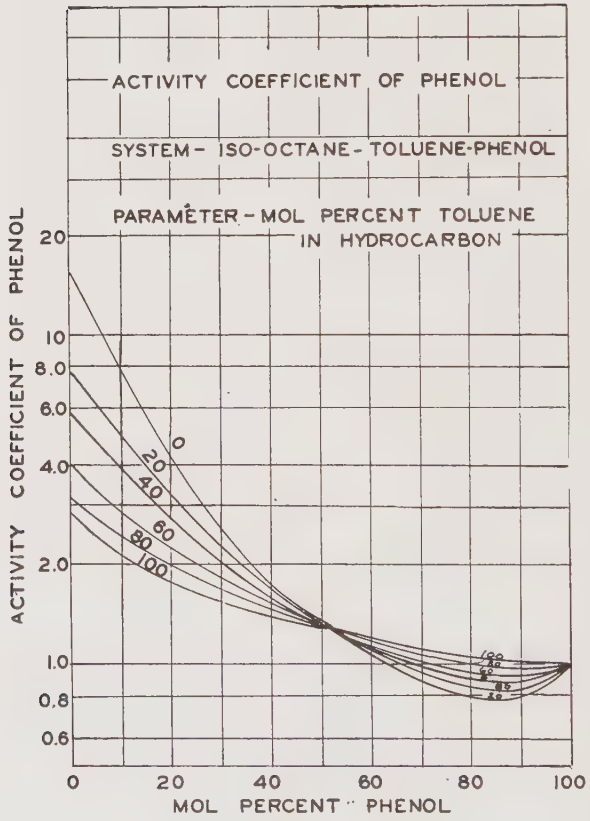
ACTIVITY COEFFICIENT OF PHENOL
SYSTEM - ISO-OCTANE - TOLUENE-PHENOL
PARAMETER - MOL PERCENT TOLUENE IN HYDROCARBON
ACTIVITY COEFFICIENT OF PHENOL
20
10
8.0
6.0
4.0
2.0
1.0
0.8
0.6
0
20
40
60
80
100
0
20
40
60
80
100
MOL PERCENT PHENOL

FIG. 12.

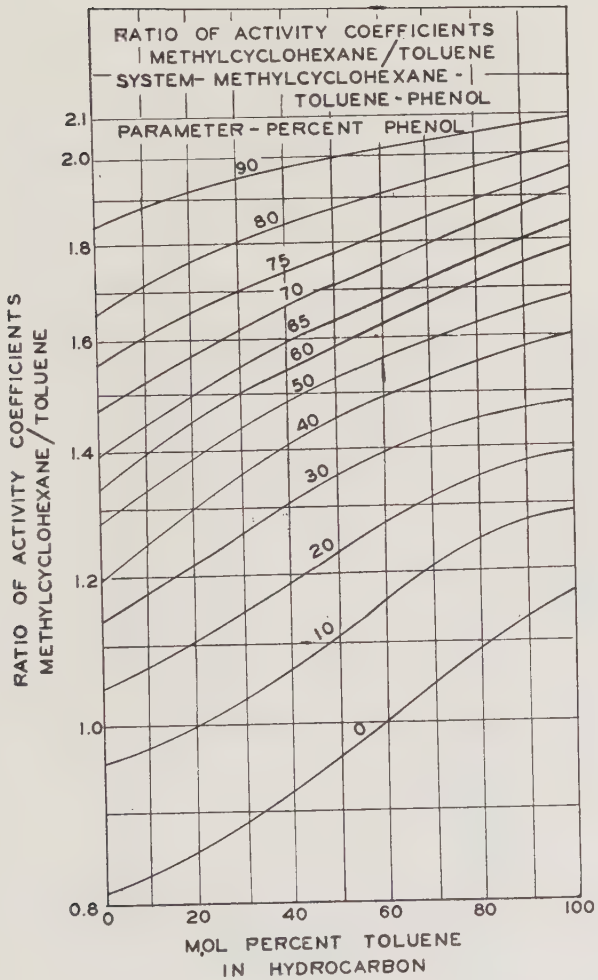
RATIO OF ACTIVITY COEFFICIENTS
METHYLCYCLOHEXANE/TOLUENE
SYSTEM- METHYLCYCLOHEXANE - TOLUENE - PHENOL
PARAMETER - PERCENT PHENOL
90
80
75
70
65
60
50
40
30
20
10
0
2.1
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0
20
40
60
80
100
RATIO OF ACTIVITY COEFFICIENTS METHYLCYCLOHEXANE/TOLUENE
MOL PERCENT TOLUENE IN HYDROCARBON

FIG. 13.

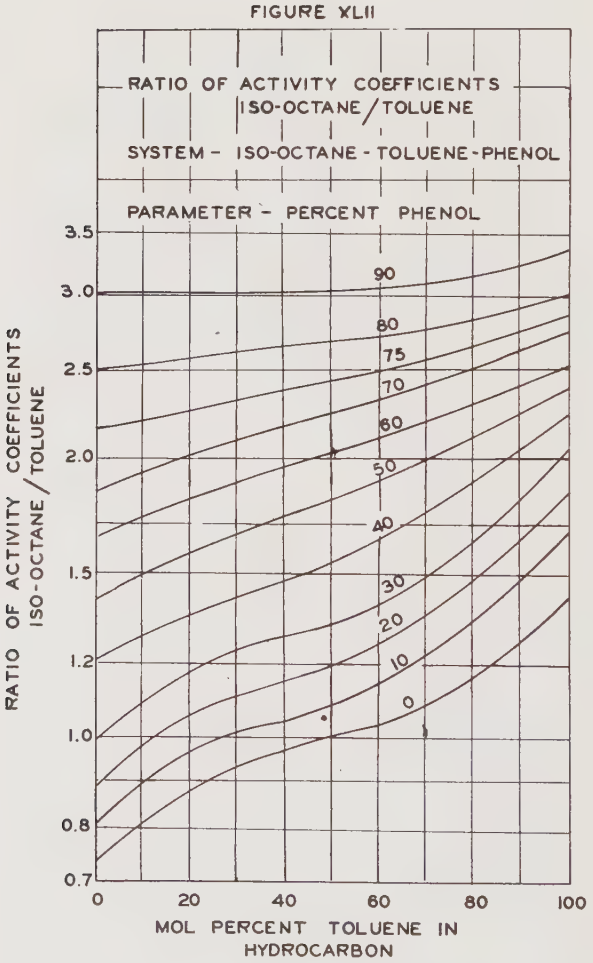
FIGURE XLII
RATIO OF ACTIVITY COEFFICIENTS
ISO-OCTANE / TOLUENE
SYSTEM - ISO-OCTANE - TOLUENE - PHENOL
PARAMETER - PERCENT PHENOL
RATIO OF ACTIVITY COEFFICIENTS
ISO-OCTANE / TOLUENE
3.5
3.0
2.5
2.0
1.5
1.2
1.0
0.8
0.7
90
80
75
70
60
50
40
30
20
10
0
0
20
40
60
80
100
MOL PERCENT TOLUENE IN
HYDROCARBON

FIG. 14.

Extrapolated activity coefficients for methylcyclohexane and isooctane in binary solutions with phenol were obtained by extrapolating Figures 8 and 11 to zero per cent toluene. There data are listed in Table XIV.

TABLE XIII.—ACTIVITY COEFFICIENT OF TOLUENE IN TOLUENE-PHENOL MIXTURES

Mole % Toluene in Liquid	Activity Coefficient of Toluene		
	From Binary Data	From Ternary Data Extrapolated to Zero Per Cent Non-Aromatic	
		*	†
10	1.98	2.1	2.16
20	1.64	1.64	1.63
30	1.435	1.43	1.43
40	1.30	1.3	1.3
50	1.19	1.18	1.19
60	1.1	1.07	1.08
70	1.05	1.03	1.04
80	1.025	1.02	1.02
90	1.007	1.005	1.01

* From system Toluene-Methylcyclohexane-Phenol.
† From system Toluene-Isooctane-Phenol.

TABLE XIV.—ACTIVITY COEFFICIENTS IN BINARY SOLUTION WITH PHENOL OBTAINED BY EXTRAPOLATION OF TERNARY DATA

Mole % Phenol	Methylcyclohexane		Isooctane	
	Temp. ° F.	Activity Coefficient	Temp. ° F.	Activity Coefficient
10	221	1.08	212	1.02
20	228	1.15	216	1.07
30	232	1.20	219	1.13
40	236	1.26	221	1.30
50	238	1.42	223	1.53
60	243	1.60	225	1.88
70	249	1.77	227	2.30
75	256	2.03	228	2.82
80	262	2.23	230	3.70
85	274	2.60	233	4.48
90	290	3.00	245	5.45

The activity coefficients for phenol in the ternary systems showed negative deviations from Raoult's Law over a considerable range of composition and were not susceptible to extrapolation. Therefore, the con-

stants for the systems methylcyclohexane-phenol and isooctane-phenol were calculated from straight lines drawn through the hydrocarbon points only, the reciprocal of the slopes of these lines giving the $\frac{a_{21}}{b_1^{1.5}}$ constants and the intercept, being equal to the product $\left(\frac{b_1^{1.5}}{a_{21}}\right)\left(\frac{b_2}{b_1}\right)$, giving the constant $\frac{b_2}{b_1}$ when divided by the slope. These constants are listed in Table XII. The activity coefficients for phenol were then calculated from these constants, since

$$\frac{a_{21}}{b_1^{1.5}} = \left(\frac{a_{21}}{b_2^{1.5}}\right)\left(\frac{b_2}{b_1}\right)^{1.5}$$

and the resulting curves compared with the experimental values for phenol as shown in Figure 6. The agreement between the calculated and experimental values is fair for the system isooctane-phenol and poorer for the system methylcyclohexane-phenol. This may be due either to errors in the relatively difficult equilibrium determinations for these systems or to the inapplicability of the equations to the correlation of the phenol data for these systems (see Addendum to Section I).

General Equation for Aromatic-Non-Aromatic Hydrocarbon Systems

The constants for the binary equations were evaluated by the methods described above from published data on the systems toluene-methylcyclohexane,[11] toluene-*n*-heptane,[1] toluene-*n*-octane,[1] benzene-*n*-hexane,[13] benzene-methylcyclohexane [5] and benzene-cyclohexane.[12]

From these constants, listed in Table XV, and the constants for the system isooctane-toluene listed in Table XII the following empirical equation has been developed for activity coefficients in aromatic-non-aromatic hydrocarbon solutions.

$$T \log \gamma_1 = \frac{K^2}{\left[1.00 + \frac{x_1}{x_2}\right]^2} \qquad (4)$$

where T = equilibrium temperature ° R.
γ_1 = activity coefficient of component 1
x_1, x_2 = mole fractions of components 1 and 2

$$K = 55.1 - 56.2 \log \frac{T_B}{100}$$

T_B = atmospheric boiling point of component in ° R.

The equation has the general form of equations (1) and (2). As presented above, it applies either to the aromatic or non-aromatic compound. The equation should be

$$T \log \gamma_1 = \frac{K_1^2}{\left[\frac{K_1^2}{K_2^2} + \frac{x_1}{x_2}\right]^2}$$

for thermodynamic consistency but equation (4) represents the data more closely. The maximum deviation from experimental data is less than 5%. The equation is of value where time and equipment are not available to obtain experimental data, or where, as with higher boiling aromatics and paraffins, it is difficult to isolate individual components for experimental work.

TABLE XV.—CONSTANTS FOR EQUATION OF STATE
Literature Binary Systems

LITERATURE BINARY SYSTEMS	$\frac{a_{21}}{b_1^{3/2}}$	$\frac{b_2}{b_1}$	$\frac{a_{12}}{b_2^{3/2}}$	$\frac{b_1}{b_2}$
(11)				
(1) Toluene	+6.9	.935		
(2) Methylcyclohexane			—7.8	1.09
(1)				
(1) Toluene	+10.0	1.15		
(2) *n*-Heptane			—7.8	.86
(1)				
(1) Toluene	+7.8	1.09		
(2) *n*-Octane			—8.2	.87
(3)				
(1) Benzene	+10.7	1.02		
(2) *n*-Hexane			—11.0	1.00
(5)				
(1) Benzene	+10.0	1.00		
(2) Methylcyclohexane			—10.0	1.00
(2)				
(1) Benezen	+10.3	1.00		
Cyclohexane			—10.3	1.00

Activity Coefficient of Phenol in Phenol-Paraffin Systems

In the rectifying section of the extractive distillation tower of a toluene purification unit, phenol appears in dilute concentration in a mixture of toluene, methylcyclohexane and various paraffin hydrocarbons. It is desirable, therefore, to investigate the effect of paraffin boiling point on the activity coefficient of phenol. The available data include nine points on the system phenol-isooctane reliable up to a concentration of 10% phenol, three points in the system isononane-phenol at phenol concentrations of zero to 3%, and the activity coefficient of phenol at zero concentration in a paraffinic cut boiling at 230° F.

From the data on the system isooctane-phenol the value of $b_2/b_1 = (0.62)$ was determined. This value was assumed to apply to the other phenol-paraffin systems. From activity coefficients at zero phenol concentration and the above value of b_2/b_1, values of $\frac{a_{21}}{b_1^{1.5}}$ were established for all three systems. From these data, presented in Table XVI, the following

general equation was developed for the phenol activity coefficient at dilute concentrations in phenol-paraffin systems.

$$T \log \gamma_1 = \frac{2.60\,(T_B) - .00319\,(T_B)^2}{\left[.62 + \frac{x_1}{x_2}\right]} \qquad (5)$$

T = equilibrium temperature ° R.
γ_1 = activity coefficient of phenol
T_B = atmospheric boiling point of the paraffin hydrocarbon, ° R.

TABLE XVI.—ACTIVITY COEFFICIENT OF PHENOL

Phenol-Paraffin Binary Solutions

System	Phenol Concentration	Activity Coefficient	Constants for Equation of State $\frac{a}{b^{3/2}}$	Constants for Equation of State $\frac{b_2}{b_1}$
Isooctane-Phenol	0	15.8	17.5	0.620
230° F. Paraffin-Phenol †	0	10.5	16.4	0.620*
Isononane-Phenol	0	6.7	15.05	0.620*

* Assumed from data for Phenol-Isooctane.
† Private communication.

Later data obtained for the system phenol-*n*-hexane agree with equation (5) and indicate that it can be applied to systems involving phenol and paraffins boiling over the range from 156-260° F.

The equation was put in convenient form for use by substituting the equilibrium temperature for the boiling temperature of the paraffin in equation (5). For dilute phenol-paraffin solutions at or near atmospheric pressure the error involved by this substitution is slight. Figure 15 shows equation (5) in graphical form.

The activity coefficient of phenol in mixtures of toluene, methylcyclohexane and paraffins may be determined from Figure 15 on the basis of the following three assumptions:

1. In the low concentrations in which it is usually present (less than 10%) methylcyclohexane can be considered equivalent to a paraffin boiling at 215° F. as far as its effect on the phenol activity coefficient is concerned.

2. At the low toluene concentration usually present in the rectifying section (1 to 15%) the effect of toluene on the activity coefficient of phenol in dilute solution is additive on a molal basis; e.g., consider a solution containing 1% phenol dissolved in a mixture of 5% toluene and 95% paraffin. The activity coefficient of phenol equals $.05x$ (activity coefficient of phenol in 1% phenol-toluene solution) plus $.95x$ (activity coefficient of phenol in 1% phenol-paraffin solution).

3. The activity coefficient of phenol in dilute solution in various paraffin hydrocarbons is solely a function of temperature and phenol concentration. Since the structures of the various paraffins in a narrow boiling range are practically identical as compared with the difference in structure between any paraffin and phenol, this assumption is logical.

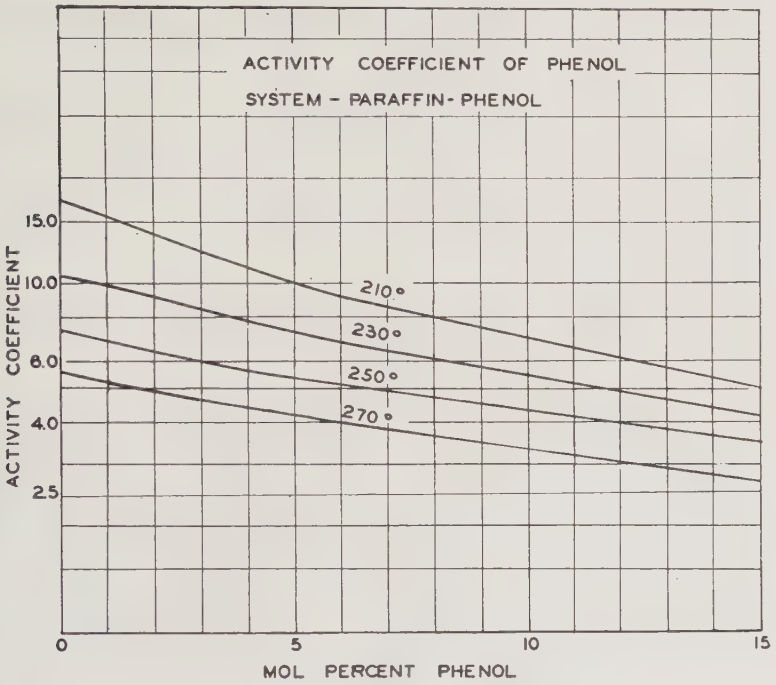

FIG. 15.

Ternary Systems

The experimental data for the ternary systems isooctane-toluene-phenol and methylcyclohexane-toluene-phenol were correlated by the ternary equations (6), (7) and (8) previously suggested [17]

$$T \ln \gamma_1 = \left[\frac{\frac{a_{21}}{b_1^{1.5}} x_2 + \frac{a_{31}}{b_1^{1.5}} x_3}{x_1 + \frac{b_2}{b_1} x_2 + \frac{b_3}{b_1} x_3} \right]^2 \qquad (6)$$

$$T \ln \gamma_2 = \left[\frac{\frac{a_{12}}{b_2^{1.5}} x_1 + \frac{a_{32}}{b_2^{1.5}} x_3}{\frac{b_1}{b_2} x_1 + x_2 + \frac{b_3}{b_2} x_3} \right]^2 \qquad (7)$$

$$T \ln \gamma_3 = \left[\frac{\frac{a^{13}}{b_3^{1.5}} x_1 + \frac{a_{23}}{b_3^{1.5}} x_2}{\frac{b_1}{b_3} x_1 + \frac{b_2}{b_3} x_2 + x_3} \right]^2 \qquad (8)$$

The constants in these equations may be evaluated from binary data, or from ternary data.

For thermodynamic consistency, according to the Gibbs-Duhem equation, the constants should satisfy the following equations

$$\frac{b_1}{b_3} = \left(\frac{b_1}{b_2}\right)\left(\frac{b_1}{b_3}\right) \tag{9}$$

and

$$b_1 a_{23} + b_2 a_{31} + b_3 a_{12} = 0 \tag{10}$$

which can be written

$$\frac{a_{23}}{b_3^{1.5}}\left(\frac{b_3}{b_1}\right)^{1.5} + \left(\frac{b_2}{b_1}\right)\frac{a_{31}}{b_1^{1.5}} + \frac{b_3}{b_1}\,\frac{a_{12}}{b_2^{1.5}}\left(\frac{b_2}{b_1}\right)^{1.5} = 0$$

Prediction of Ternary Relations from Binary Data

From equations (9) and (10) it is apparent that if the data for two of the binary mixtures involved are available, the constants for the third may be computed. Where the data for the three binary mixtures are available, there may frequently be some inconsistency between the values calculated from the experimental data and those calculated from the other two binary systems by equations (9) and (10). This inconsistency may be large or small and is due either to errors in the experimental data or to the inapplicability of the equations to the systems involved. Where the inconsistency is large and the binary data appear to be reliable, the binary constants probably cannot be used to predict ternary relationships. However, where the inconsistency is small, prediction of ternary equilibrium may be feasible. At the present time, while this procedure has been shown to be satisfactory for several ternary systems, the number of systems investigated is not sufficient to establish the limitations of the equations in predicting ternary equilibria from binary data. However, for several systems involving two hydrocarbons and a solvent it has been possible to calculate from binary data, ternary equilibria which agree fairly well with experimental ternary data.

The signs of the a terms in equations (6), (7) and (8) are important, and cannot be determined from the binary equations. However, they can be determined from the van der Waals' constants and equation (11).

$$a_{kl} = \left(b_k\sqrt{a_i} - b_i\sqrt{a_k}\right)\left(\frac{8f}{27R}\right)^{1/2} \tag{11}$$

This relationship is not quantitative, but it can be used to predict the sign of x. The critical constants, van der Waals' constants, and the signs for the various terms are listed in Table XVIII for the binary systems involved in the mixtures isooctane-toluene-phenol and methylcyclohexane-toluene-phenol. The signs for the constants listed in Table XII and XV were obtained in the same manner. The critical constants for toluene and phenol were obtained from the International Critical Tables [6]; those for methylcyclohexane and isooctane were calculated as described by Meissner and Redding.[9]

TABLE XVII.—CRITICAL AND VAN DER WAALS' CONSTANTS

	Toluene	Methyl-cyclo-hexane	Isooctane	Phenol
Critical temperature ° R.	1069	1054*	974*	1245
Critical pressure *PSI*	611	479*	343*	890
Critical volume cu.ft. per lb. mole	5.05	6.12*	7.87*	6.12
van der Waals' *a*	4.67×10^4	5.38×10^4	6.38×10^4	6.04×10^4
van der Waals' *b*	1.68	2.04	2.62	1.585
System: Toluene-Isooctane Sign of α †	+		−	
System: Toluene-Methylcyclo-hexane Sign of α †	+	−		
System: Phenol-Toluene Sign of α †	−			+
System: Phenol-Methylcyclo-hexane Sign of α †		−		+
System: Phenol-Isooctane Sign of α†			−	+

* Calculated by method of Meissner and Redding.[9]

† $$\alpha_{21} = \left[b_2\sqrt{a_1} - b_1\sqrt{a_2} \right] \left[\frac{8f}{27R} \right]^{1/4}$$

For these systems the constants for the three binary systems proved to be fairly consistent, and the equations of Table XVIII were obtained by substituting the values in equations (6), (7) and (8) from Table XII. Tables XIX and XX compare activity coefficients calculated from these equations with the smoothed experimental data for Figures 7 through 12. For the hydrocarbon components the agreement is within 5% in most regions with a maximum deviation of 10%. For phenol the maximum deviation is 25%. The phenol data are somewhat irregular, and at high phenol concentrations negative deviations from Raoult's Law (activity coefficients less than one) were obtained. This may be due to analytical error, to small errors in observed equilibrium temperature, or to the fact that phenol associates in the liquid phase.

The prediction of ternary data from binary data is particularly promising for cases where samples containing three components are so difficult to analyze that even with great care errors of greater than 10% can be anticipated.

Table XVIII.—Ternary Equations of State Predicted from Binary Data

Methylcyclohexane-Toluene-Phenol

$$T \log \gamma_1 = \left[\frac{-7.8 - 20.6 \frac{x_3}{x_2}}{\frac{x_1}{x_2} + 1.08 + 0.93 \frac{x_3}{x_1}} \right]^2$$

$$T \log \gamma_2 = \left[\frac{6.9 - 14.4 \frac{x_3}{x_1}}{\frac{x_2}{x_1} + 0.93 + 0.84 \frac{x_3}{x_1}} \right]^2$$

$$T \log \gamma_3 = \left[\frac{23.5 + 19.6 \frac{x_2}{x_1}}{\frac{x_3}{x_1} + 1.08 + 1.17 \frac{x_2}{x_1}} \right]^2$$

Isooctane-Toluene-Phenol

$$T \log \gamma_1 = \left[\frac{-8.0 - 22.4 \frac{x_3}{x_2}}{\frac{x_1}{x_2} + 1.00 + 0.84 \frac{x_3}{x_2}} \right]^2$$

$$T \log \gamma_2 = \left[\frac{8.0 - 14.4 \frac{x_3}{x_1}}{\frac{x_2}{x_1} + 1.0 + 0.84 \frac{x_3}{x_1}} \right]^2$$

$$T \log \gamma_3 = \left[\frac{28.9 + 19.6 \frac{x_2}{x_1}}{\frac{x_3}{x_1} + 1.18 + 1.18 \frac{x_2}{x_1}} \right]^2$$

TABLE XIX.—COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS

Methylcyclohexane-Toluene-Phenol

Liquid Composition			Activity Coefficients					
			Methylcyclohexane		Toluene		Phenol	
Phenol	Toluene	Methylcyclohexane	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
20	20	60	1.11	1.18	1.00	1.03	2.50	2.12
20	40	40	1.19	1.21	1.00	1.00	2.24	1.98
20	60	20	1.29	1.34	1.01	1.00	2.00	1.84
40	5	55	1.26	1.13	1.01	1.01	1.67	1.10
40	10	50	1.31	1.16	1.02	1.00	1.65	1.11
40	15	45	1.34	1.30	1.03	1.00	1.63	1.20
40	30	30	1.44	1.45	1.05	1.00	1.59	1.30
40	45	15	1.53	1.56	1.08	1.00	1.55	1.35
40	50	10	1.56	1.66	1.09	1.04	1.53	1.37
40	55	5	1.60	1.70	1.11	1.05	1.52	1.38
60	5	35	1.67	1.58	1.16	1.13	1.26	0.75
60	10	30	1.80	1.66	1.18	1.14	1.25	0.80
60	20	20	1.88	1.80	1.21	1.16	1.23	0.90
60	30	10	1.98	2.00	1.25	1.21	1.22	1.01
60	35	5	2.04	2.12	1.28	1.24	1.21	1.10
80	2	18	2.56	2.40	1.52	1.38	1.06	0.65
80	5	15	2.65	2.50	1.56	1.40	1.06	0.88
80	10	10	2.72	2.70	1.60	1.45	1.05	0.80
80	15	5	2.83	2.98	1.64	1.52	1.05	0.70
80	18	2	3.00	3.20	1.67	1.57	1.05	1.00

TABLE XX.—COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS

Isooctane-Toluene-Phenol

Liquid Composition			Activity Coefficients					
			Isooctane		Toluene		Phenol	
Phenol	Toluene	Isooctane	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
20	20	60	1.14	1.13	1.01	1.03	3.20	3.10
20	40	40	1.23	1.21	1.00	1.00	2.80	2.55
20	60	20	1.35	1.42	1.00	1.00	2.20	2.10
40	5	55	1.38	1.30	1.00	1.03	2.22	1.77
40	10	50	1.42	1.35	1.01	1.01	2.13	1.70
40	15	45	1.48	1.39	1.02	1.00	2.10	1.53
40	30	30	1.62	1.51	1.04	1.00	1.91	1.50
40	45	15	1.84	1.85	1.07	1.01	1.72	1.50
40	50	10	1.92	2.04	1.08	1.04	1.60	1.49
40	55	5	1.98	2.26	1.10	1.05	1.48	1.48
60	5	35	2.16	2.02	1.15	1.12	1.45	1.05
60	10	30	2.26	2.12	1.17	1.13	1.41	1.06
60	20	20	2.46	2.35	1.22	1.16	1.34	1.08
60	30	10	2.67	2.84	1.25	1.20	1.28	1.12
60	35	5	2.82	3.05	1.29	1.24	1.25	1.15
80	2	18	4.00	3.76	1.53	1.48	1.10	0.78
80	5	15	4.10	3.91	1.55	1.49	1.09	0.90
80	10	10	4.25	4.05	1.58	1.51	1.08	0.80
80	15	5	4.36	4.20	1.62	1.54	1.06	1.00
80	18	2	4.65	4.80	1.69	1.62	1.05	1.01

Evaluation of Constants from Ternary Data

As has been shown,[17] plots of $(T \ln \gamma_1)^{-0.5}$ versus x_1/x_2 or x_1/x_3 with a parameter of x_3/x_2 or x_2/x_3 respectively, should give a family of straight lines intersecting at a common point. Similar relations hold for plots of $(T \ln \gamma_2)^{-0.5}$ versus x_2/x_1 or x_3/x_1 and $(T \ln \gamma_3)^{-0.5}$ versus x_3/x_1 or x_3/x_2. Thus, an equation may be obtained for the activity coefficient of a

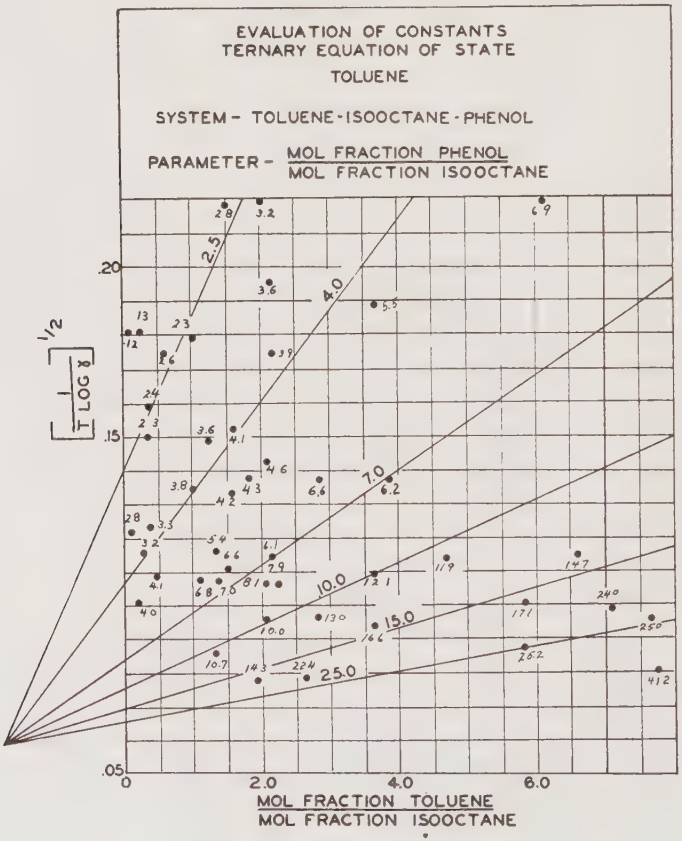

Fig. 16.

given component by fitting a family of such lines to the ternary data. For a ternary system, there should be three such families of lines and thermodynamic consistency can be obtained if the three families of lines are fitted to the data in such a way that the derived constants satisfy equations (9) and (10).

It has been found that, where thermodynamic consistency is desired, a good procedure is to evaluate the constants for equations (6), (7) and (8) from binary data, then draw the lines of constant x_3/x_2 obtained from

the equations on a graph containing the plotted ternary points. The lines can then be adjusted slightly to give a better fit with the ternary data, and the constants modified accordingly, maintaining thermodynamic consistency. In this manner Figures 16-19 were obtained for the hydrocarbon components in the systems isooctane-toluene-phenol and methylcyclohexane-toluene-phenol. Since the phenol data were somewhat irregular,

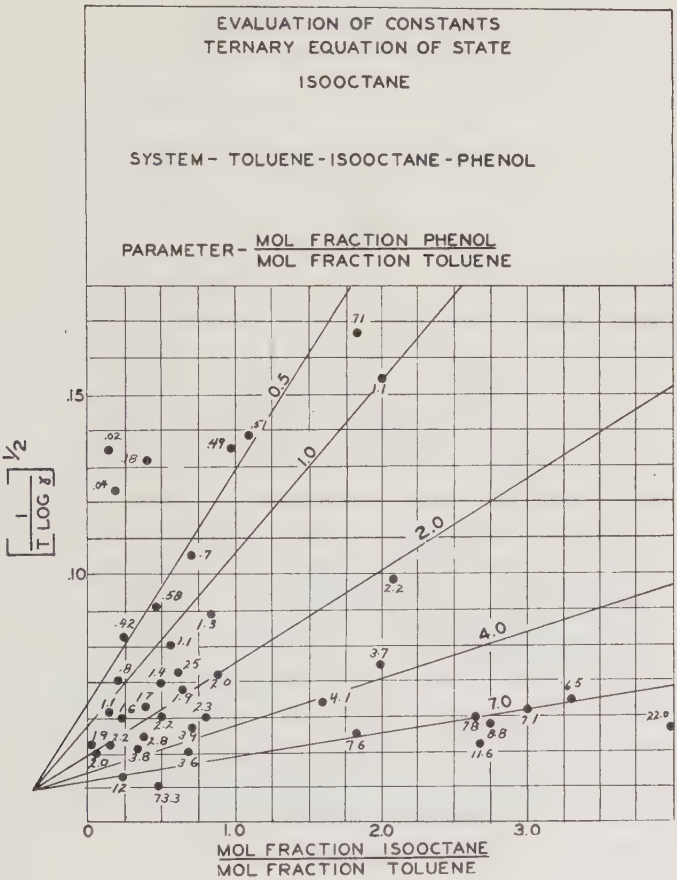

Fig. 17.

the constants for the phenol equations were calculated from the constants for the hydrocarbon components by equations (9) and (10). The equations obtained are shown in Table XXI. Tables XXII and XXIII compare the calculated activity coefficients with the smoothed experimental values of Figures 7 through 12. The agreement is somewhat better than was obtained with the values predicted from binary data (Tables XIX and XX).

The evaluation of the constants in this manner, adjusting the straight lines to fit the data, to intersect in a single point, and still give thermodynamically consistent constants from three different graphs, is somewhat tedious, and may not always be necessary. For practical purposes, it is often sufficient to disregard the interrelation between the three families of

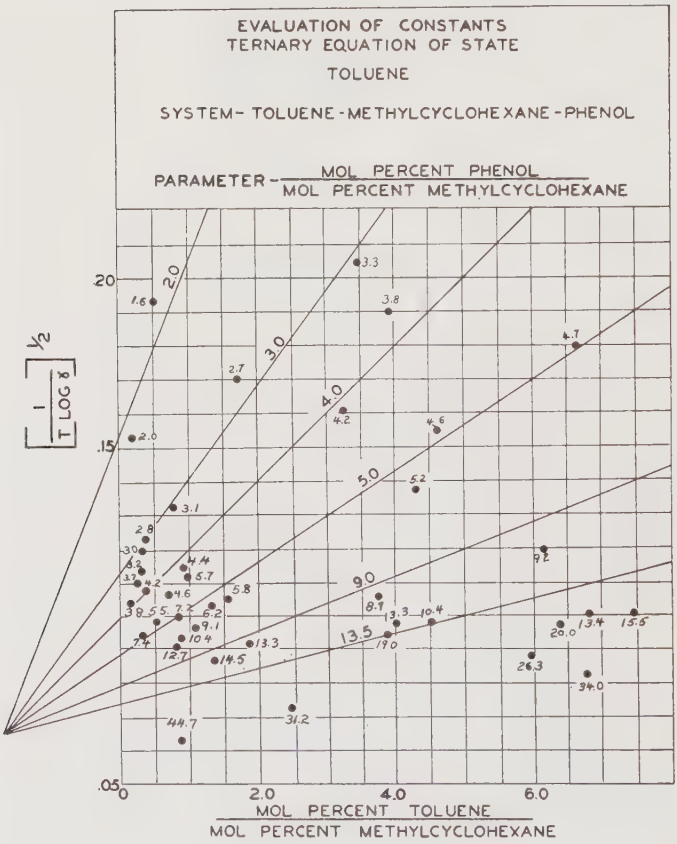

FIG. 18.

curves and to fit each family of lines to the ternary equation empirically. The equations so derived will not be thermodynamically consistent but may be used to reproduce and smooth experimental data for practical use. In this case, the equations would not necessarily represent activity coefficients in the thermodynamic sense, so that they might be called "correlating factors" or "correction factors."

In this manner equations which fit the data very closely can be obtained in a relatively short time. These equations are quite satisfactory for equilibrium calculations in the region in which the data have been obtained. However, they probably should not be used to extrapolate the data or to predict other thermodynamic functions.

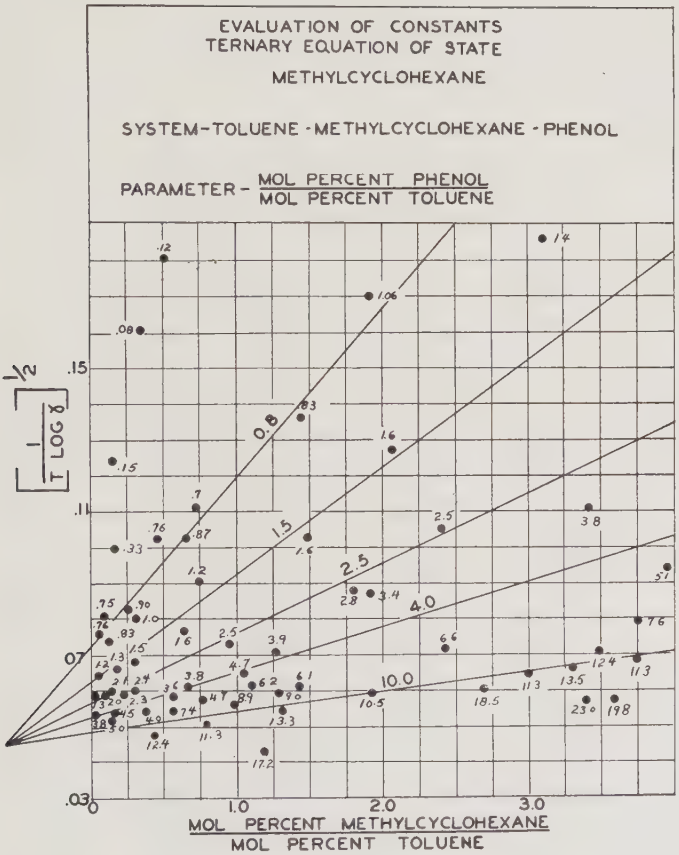

FIG. 19.

This type of equation is particularly useful where a comparison between various solvents as extractive distillation separating agents is desired. Ternary data can be obtained over the range of potential operating solvent concentrations (usually 50-80% solvent in the liquid phase) and these empirical equations can be used to smooth the data. At the relatively high solvent concentrations usually encountered the activity coefficient of the solvent will usually be negligible so that no equation need be obtained for it.

TABLE XXI.—TERNARY EQUATIONS OF STATE

Methylcyclohexane-Toluene-Phenol

Methylcyclohexane-Toluene-Phenol

$$T \log \gamma_1 = \left[\frac{-6.2 - 18.0 \frac{x_3}{x_2}}{\frac{x_1}{x_2} + 0.90 + 0.80 \frac{x_3}{x_2}} \right]^2$$

$$T \log \gamma_2 = \left[\frac{7.2 - 13.6 \frac{x_3}{x_1}}{\frac{x_2}{x_1} + 1.11 + 0.90 \frac{x_3}{x_1}} \right]^2$$

$$T \log \gamma_3 = \left[\frac{25.2 + 16.0 \frac{x_2}{x_1}}{\frac{x_3}{x_1} + 1.25 + 1.10 \frac{x_2}{x_1}} \right]^2$$

Isooctane-Toluene-Phenol

$$T \log \gamma_1 = \left[\frac{-10 - 21.0 \frac{x_3}{x_2}}{\frac{x_1}{x_2} + 1.0 + 0.8 \frac{x_3}{x_2}} \right]^2$$

$$T \log \gamma_2 = \left[\frac{10 - 13.0 \frac{x_3}{x_1}}{\frac{x_2}{x_1} + 1.0 + 0.80 \frac{x_3}{x_1}} \right]^2$$

$$T \log \gamma_3 = \left[\frac{29.3 + 18.2 \frac{x_2}{x_1}}{\frac{x_3}{x_1} + 1.25 + 1.25 \frac{x_2}{x_1}} \right]^2$$

TABLE XXII.—COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS

Methylcyclohexane-Toluene-Phenol

Liquid Composition			Activity Coefficients					
			Methylcyclohexane		Toluene		Phenol	
Phenol	Toluene	Methylcyclohexane	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
20	20	60	1.12	1.18	1.02	1.03	2.30	2.12
20	40	40	1.19	1.21	1.00	1.00	2.06	1.98
20	60	20	1.29	1.34	1.00	1.00	1.84	1.84
40	5	55	1.23	1.13	1.00	1.01	1.88	1.10
40	10	50	1.27	1.16	1.00	1.00	1.68	1.11
40	15	45	1.31	1.30	1.00	1.00	1.64	1.20
40	30	30	1.42	1.45	1.03	1.00	1.53	1.30
40	45	15	1.57	1.56	1.05	1.00	1.43	1.35
40	50	10	1.64	1.66	1.07	1.04	1.39	1.37
40	55	5	1.69	1.70	1.085	1.05	1.37	1.38
60	5	35	1.68	1.58	1.09	1.13	1.31	0.75
60	10	30	1.73	1.66	1.11	1.14	1.27	0.80
60	20	20	1.87	1.80	1.15	1.16	1.22	0.90
60	30	10	2.06	2.00	1.20	1.21	1.18	1.01
60	35	5	2.16	2.12	1.23	1.24	1.16	1.10
80	2	18	2.54	2.40	1.375	1.38	1.08	0.65
80	5	15	2.62	2.50	1.42	1.40	1.07	0.88
80	10	10	2.74	2.70	1.45	1.45	1.06	0.80
80	15	5	2.92	2.98	1.50	1.52	1.05	0.70
80	18	2	3.06	3.20	1.54	1.57	1.04	1.00

TABLE XXIII.—COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS

Isooctane-Toluene-Phenol

Liquid Composition			Activity Coefficients					
			Isooctane		Toluene		Phenol	
Phenol	Toluene	Isooctane	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
20	20	60	1.16	1.13	1.055	1.03	2.84	3.10
20	40	40	1.27	1.21	1.00	1.00	2.50	2.55
20	60	20	1.48	1.42	1.00	1.00	1.90	2.10
40	5	55	1.34	1.30	1.00	1.03	2.07	1.77
40	10	50	1.41	1.35	1.00	1.01	1.95	1.70
40	15	45	1.47	1.39	1.00	1.00	1.90	1.53
40	30	30	1.66	1.51	1.02	1.00	1.68	1.50
40	45	15	1.94	1.85	1.055	1.01	1.55	1.50
40	50	10	2.10	2.04	1.07	1.04	1.46	1.49
40	55	5	2.21	2.26	1.086	1.05	1.40	1.48
60	5	35	2.06	2.02	1.08	1.12	1.38	1.05
60	10	30	2.18	2.12	1.10	1.13	1.35	1.06
60	20	20	2.45	2.35	1.16	1.16	1.29	1.08
60	30	10	2.86	2.84	1.22	1.20	1.23	1.12
60	35	5	3.13	3.05	1.26	1.24	1.20	1.15
80	2	18	3.80	3.76	1.43	1.48	1.10	0.78
80	5	15	3.92	3.91	1.46	1.49	1.08	0.90
80	10	10	4.14	4.05	1.52	1.51	1.07	0.80
80	15	5	4.36	4.20	1.59	1.54	1.05	1.00
80	18	2	4.66	4.80	1.62	1.62	1.04	1.01

Ternary Systems Including Sludge

In the extractive distillation process for the purification of toluene, the phenol forms a sludge through reaction with the small amounts of diolefins in the hydrocarbon charge. This sludge consists largely of a phenol with an unsaturated side chain. When purified, it is an amber liquid, miscible with hydrocarbons at ordinary temperatures. Since this sludge constitutes zero to 50% of the phenol during normal operation, it is important to establish the effect of the sludge on aromatic-non-aromatic hydrocarbon vapor-liquid equilibria.

From Table XXIV it can be seen that the ratio of activity coefficients of non-aromatic to toluene in the presence of 50 to 75 mole % sludge is practically the same as in the binary (sludge free) systems at the same relative aromatic-non-aromatic concentration. Therefore, the sludge can be considered an inert component carried along with the phenol.

TABLE XXIV.—ACTIVITY COEFFICIENTS IN SYSTEMS INCLUDING SLUDGE

Sample	Mole Fraction Sludge in Liquid	Mole Fraction Toluene in Liquid Hydrocarbon	Activity Coefficients	
			Toluene	Methylcyclohexane
SM-1	61.47	79.9	1.325	1.535
SM-2	52.12	44.4	1.27	1.245
			Activity Coefficients	
			Toluene	Isooctane
SP-1	63.5	85.4	1.41	1.75
SP-2	71.05	14.6	1.445	1.68

	Ratio of Activity Coefficients $\frac{\text{Methylcyclohexane}}{\text{Toluene}}$	Ratio of Activity Coefficients Obtained for Binary (Sludge Free) Data $\frac{\text{Methylcyclohexane}}{\text{Toluene}}$
SM-1	1.16	1.11
SM-2	.98	.95
	Ratio of Activity Coefficients $\frac{\text{Isooctane}}{\text{Toluene}}$	$\frac{\text{Isooctane}}{\text{Toluene}}$
SP-1	1.24	1.18
SP-2	1.16	1.12

Isononane-Toluene-Phenol

In the purification of toluene from petroleum by extractive distillation, the toluene is fractionated from methylcyclohexane and from various paraffins in its boiling range in the presence of 40.0% or more phenol on the trays. Therefore, it is important to test whether the correlations

developed for the system phenol-toluene-isooctane (boiling point, 211° F.) apply to the data obtained for the system phenol-toluene-isononane (boiling point, 255° F.). These latter data were all obtained at phenol concentrations above 40% in the liquid phase. Table XXV compares experimental activity coefficients with those obtained from Figures 7 through 14. The agreement is as good as was obtained by comparing experimental data for the system isooctane-toluene-phenol with the smoothed curves. Therefore, Figures 7 through 14 and the various correlating equations of Tables XVIII and XXI can be applied to mixtures of toluene, phenol, and paraffin hydrocarbons boiling between 211° and 255° F., as long as the phenol concentration in the liquid phase is more than 40%.

Quaternary Systems

The quaternary data were obtained to investigate the applicability of the ternary data and correlations to multicomponent systems. Table XXVI compares the experimental activity coefficients with those obtained from the smoothed ternary data (Figures 7 through 14). The agreement is within the accuracy of the experimental data. Thus the correlations developed for the ternary data can be legitimately applied to the multicomponent systems encountered in the commercial purification of toluene by extractive distillation.

Conclusions

Vapor-liquid equilibrium data have been presented for binary, ternary, and quaternary systems involving toluene, methylcyclohexane, paraffin hydrocarbons in the toluene boiling range, and phenol.

Equations have been presented which satisfactorily correlate the experimental data. In addition, general equations have been developed for equilibria in binary aromatic-non-aromatic systems and for phenol activity coefficients in phenol-paraffin hydrocarbon binary systems.

It appears possible that ternary equilibria may be predicted from binary data, with reasonable accuracy.

The data and correlations which have been developed are satisfactory for the study of the equilibrium relationships occurring in a commercial unit for the purification of toluene from petroleum.

APPENDIX I

Analytical Procedures

Phenol

On most of the samples the per cent phenol was determined from the refractive indices before and after caustic washing. Figure 20 shows the relationship between the actual volume per cent and the volume per cent calculated as proportional to the refractive indices.

On samples where two liquid phases or a solid phase separated at room temperature, the per cent was determined as the weight per cent absorbed from the hot sample in concentrated caustic.

TABLE XXV.—COMPARISON OF EXPERIMENTAL AND PREDICTED ACTIVITY COEFFICIENTS

Toluene-Isononane-Phenol

AE	Per Cent Phenol	Per Cent Toluene in Hydrocarbon	Activity Coefficients: Phenol Experimental	Phenol Predicted	Toluene Experimental	Toluene Predicted	Isononane Experimental	Isononane Predicted	Isononane/Toluene Experimental	Isononane/Toluene Predicted
1	66.69	79.90	1.08	1.09	1.295	1.3	3.28	3.16	2.53	2.47
2	65.42	61.40	1.02	1.04	1.24	1.24	2.62	2.74	2.13	2.21
3	62.91	41.30	.995	1.02	1.24	1.19	2.60	2.45	2.10	2.05
4	63.20	17.65	.94	1.00	1.15	1.16	2.08	2.18	1.82	1.88
11	81.98	87.40	.95	1.02	1.71	1.64	4.80	4.74	2.81	2.92
12	81.40	76.0	.965	.97	1.54	1.56	4.33	4.40	2.81	2.85
13	80.95	21.52	.915	.82	1.436	1.48	3.91	3.95	2.72	2.64
21	62.40	82.60	1.1	1.17	1.26	1.26	3.06	3.00	2.43	2.38
22	63.70	47.50	1.01	1.05	1.24	1.20	2.63	2.51	2.12	2.08
31	69.73	83.90	.99	1.09	1.32	1.36	3.37	3.44	2.56	2.55
32	69.60	67.10	1.06	1.03	1.28	1.305	3.78	3.13	2.44	2.38
33	69.78	52.30	.97	.97	1.30	1.28	2.80	2.89	2.19	2.22
34	71.36	40.60	.885	.92	1.29	1.28	2.79	2.82	2.16	2.21
35	76.84	9.94	.95	.80	1.35	1.35	3.04	3.00	2.25	2.24
41	51.50	73.40	1.35	1.30	1.09	1.12	2.30	2.32	2.11	2.09
42	53.25	64.6	1.3	1.27	1.135	1.12	2.32	2.30	2.04	2.00
43	52.35	52.85	1.23	1.26	1.11	1.11	2.07	2.09	1.87	1.88
44	45.80	36.9	1.44	1.48	1.093	1.04	1.79	1.69	1.62	1.59
45	55.40	10.4	1.07	1.15	1.10	1.10	1.86	1.80	1.69	1.62
61	67.79	91.0	1.12	1.12	1.43	1.37	3.78	3.50	2.64	2.60
62	75.58	79.30	1.00	1.01	1.55	1.46	3.95	3.85	2.55	2.63
63	67.89	63.80	1.00	1.02	1.315	1.295	3.11	2.90	2.36	2.30
71	59.23	60.00	1.08	1.12	1.14	1.175	2.28	2.50	2.00	2.10
72	63.31	92.00	1.10	1.16	1.40	1.31	3.55	3.30	2.52	2.50
81	74.42	86.30	.97	1.06	1.40	1.44	3.80	3.88	2.71	2.70
82	74.60	68.80	.95	.98	1.41	1.40	3.475	3.55	2.46	2.52

TABLE XXVI.—COMPARISON OF EXPERIMENTAL AND PREDICTED ACTIVITY COEFFICIENTS

Toluene-Methylcyclohexane-Isooctane-Phenol

AC	Per Cent Phenol	Per Cent Toluene in Hydrocarbon	Activity Coefficients: Phenol Experimental	Phenol Predicted	Toluene Experimental	Toluene Predicted	Methylcyclohexane Experimental	Methylcyclohexane Predicted	Isooctane Experimental	Isooctane Predicted	Methylcyclohexane/Toluene Experimental	Methylcyclohexane/Toluene Predicted	Isooctane/Toluene Experimental	Isooctane/Toluene Predicted
51	68.03	79.3	1.00	1.06	1.355	1.326	2.41	2.38	3.47	3.3	1.78	1.76	2.55	2.48
52	69.07	75.7	.98	1.02	1.425	1.34	2.64	2.42	3.39	3.3	1.85	1.81	2.38	2.45
53	58.50	55.8	1.07	.98	1.14	1.16	1.845	1.75	2.485	2.35	1.62	1.59	2.18	2.05
54	65.68	51.2	.98	1.01	1.22	1.225	1.95	2.00	2.66	2.70	1.60	1.65	2.17	2.12
61	49.02	68.8	1.47	1.35	1.05	1.09	1.70	1.70	2.08	2.16	1.62	1.58	2.98	2.00
62	49.58	69.2	1.13	1.15	1.035	1.09	1.76	1.71	2.17	2.17	1.70	1.59	2.10	2.02
63	46.88	35.5	1.45	1.42	.97	1.05	1.32	1.48	1.49	1.64	1.36	1.42	1.54	1.60
64	43.75	32.4	1.49	1.50	1.01	1.05	1.36	1.43	1.565	1.55	1.345	1.37	1.55	1.51
71	46.16	76.5	1.39	1.40	1.07	1.07	1.72	1.70	2.12	2.1	1.60	1.58	1.98	1.79
72	50.36	27.6	1.23	1.31	1.07	1.08	1.51	1.50	1.78	1.78	1.41	1.41	1.66	1.65
73	54.85	31.0	1.12	1.19	1.105	1.11	1.615	1.62	1.98	2.00	1.46	1.465	1.79	1.76
74	51.40	46.1	1.26	1.30	1.09	1.09	1.625	1.63	1.981	2.00	1.49	1.51	1.82	1.79
81	10.71	46.00	3.3	3.2	1.01	1.01	1.10	1.12	1.17	1.08	1.09	1.08	1.16	1.08
82	9.79	47.90	3.6	3.9	1.01	1.01	1.21	1.12	1.08	1.07	1.20	1.10	1.07	1.08
83	12.68	14.35	4.95	5.0	1.16	1.1	1.09	1.10	1.18	1.05	.94	1.01	1.02	.95
84	11.81	11.90	7.00	5.4	1.17	1.12	1.20	1.09	1.02	1.04	1.025	.99	.872	.91
91	18.51	41.00	2.3	2.1	1.02	1.00	1.18	1.18	1.35	1.16	1.16	1.18	1.32	1.15
92	20.63	43.40	2.5	2.6	.99	1.00	1.31	1.21	1.17	1.18	1.32	1.21	1.18	1.18

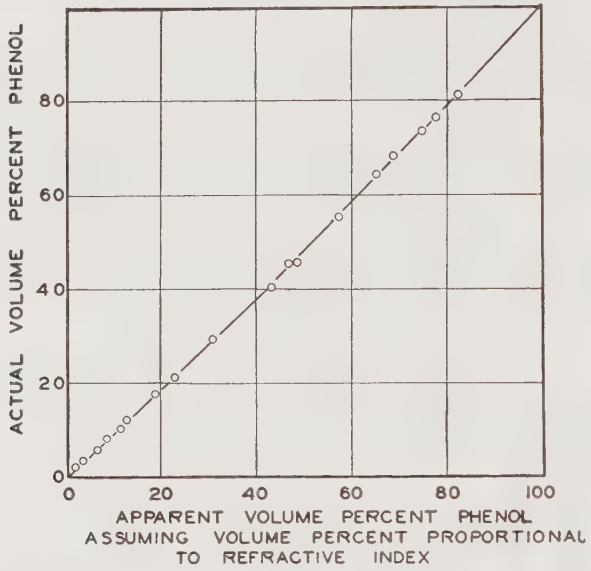

FIG. 20. Volume Per Cent Phenol in Mixtures of Phenol and Hydrocarbon.

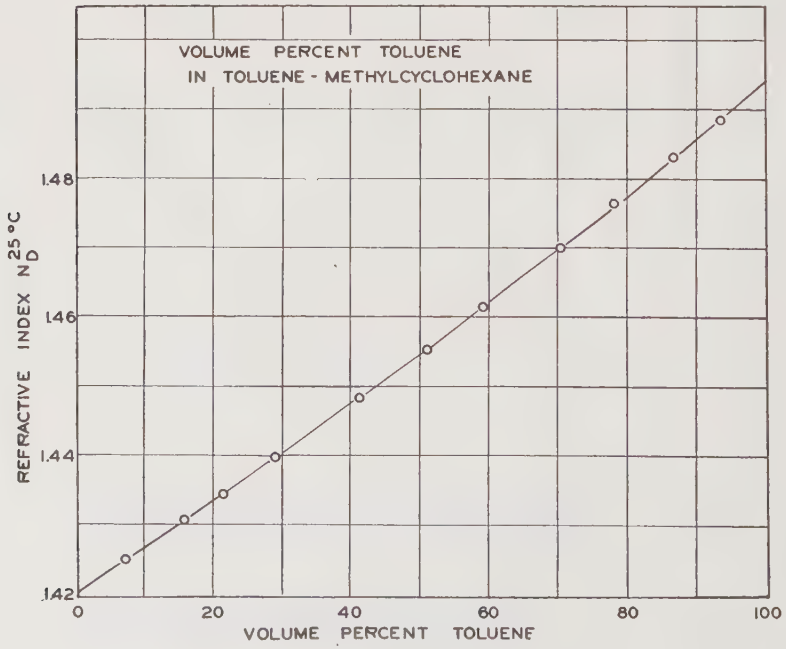

FIG. 21.

For samples containing less than 2% phenol, a titration method was used. An acidified potassium bromate-potassium bromide solution was used as a source of bromine. An excess of the solution is added and the uncombined bromine was back-titrated with sodium thiosulphate. The tribromophenol is formed, so the phenol concentration can be calculated from the bromine disappearance.

Hydrocarbons

The hydrocarbons were determined from the refractive index of the phenol free sample. For mixtures of toluene-paraffins and methylcyclohexane-paraffins the volume per cent was proportional to the refractive index. Figure 21 is a correlation between refractive index and volume per cent toluene in toluene-methylcyclohexane mixtures.

The per cent toluene in mixtures of toluene, methylcyclohexane, and paraffins was determined from the refractive index before and after the toluene was removed, using a correlation developed by Baytown Ordnance Works for this purpose. The toluene was removed by washing with 98% sulfuric acid.

Accuracy of Analytical Results

Since the limit of error in reading the refractometer was two in the fourth place, and did not vary noticeably for various mixtures, the limits of error expressed in per cent of compound varied with the difference in refractive indices, as given below:

Phenol in phenol-hydrocarbon mixtures ±.13-.42%
Toluene-isooctane mixtures ±.19%
Toluene-methylcyclohexane mixtures ±.28%
Toluene-isononane mixtures ±.21%

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ADDENDUM TO SECTION I

At the time when the original data were correlated, the lack of agreement between the experimental binary data and extrapolated ternary data, especially for the system methylcyclohexane-phenol (see Figure 6), raised some question concerning the accuracy of these binary data, especially since these data were obtained at the beginning of the work, before experimental and analytical procedures were perfected. Further, the availability of a

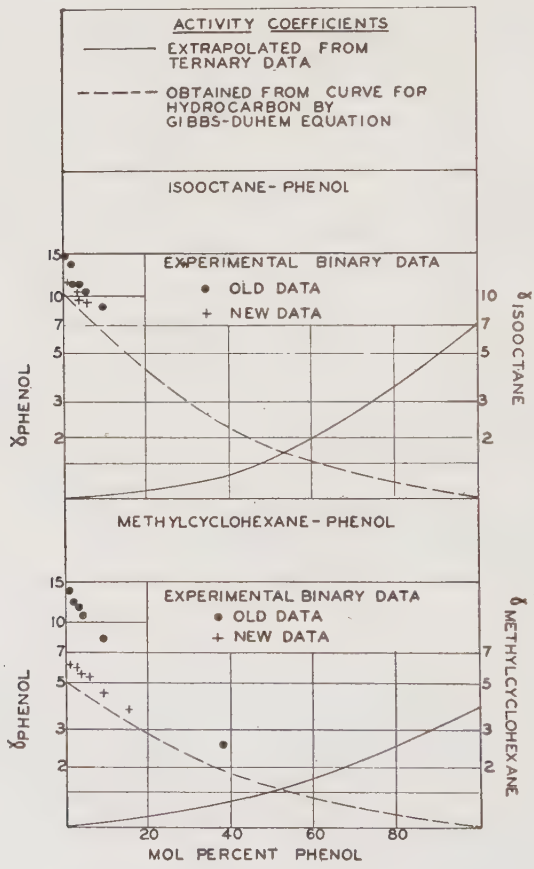

FIG. 22.

Bausch and Lomb precision refractometer made it possible to obtain much more accurate refractive indices. Therefore, four more points were obtained in the system isooctane-phenol and six more points in the system methylcyclohexane-phenol. These data are shown in Tables XXVII and XXVIII. As can be seen from Figure 22, the data for the isooctane-phenol binary system substantially check the earlier data. However, the

new data for the system methylcyclohexane-phenol are considerably different from the earlier data and show fairly good agreement with the extrapolated ternary data. The authors place considerably more reliance on the new data, and feel that the earlier data must have suffered from irregularities in still operation and/or analytical procedure.

TABLE XXVII.—VAPOR-LIQUID EQUILIBRIA

System Methylcyclohexane-Phenol

760 mm. Hg. Pressure

M-F	Equilibrium Temp. ° F.	Mole % Liquid	Phenol Vapor	Activity Coefficients	
				Phenol	Methylcyclohexane
10	217	16.31	3.32	3.46	1.090
11	216	9.80	2.62	4.54	1.050
12	215	6.50	2.08	5.55	1.020
13	215	5.14	1.72	5.56	1.015
14	214	2.50	0.83	5.91	1.005
15	214	1.69	0.58	6.10	1.005

TABLE XXVIII.—VAPOR-LIQUID EQUILIBRIA

System Isooctane-Phenol

760 mm. Hg. Pressure

AP	Equilibrium Temp. ° F.	Mole % Liquid	Phenol Vapor	Activity Coefficients	
				Phenol	Isooctane
10	213	4.85	2.50	9.2	1.010
11	212	2.50	1.33	9.6	1.005
12	212	2.32	1.30	10.1	1.005
13	212	1.22	.83	12.7	1.000

SECTION II

APPLICATION OF EXPERIMENTAL VAPOR-LIQUID EQUILIBRIA TO AN ANALYSIS OF THE OPERATION OF A COMMERCIAL UNIT FOR THE PURIFICATION OF TOLUENE FROM PETROLEUM

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(Junior Members)

Abstract

The vapor-liquid equilibria presented in the previous paper are applied to two tests on the toluene purification unit of the Pan-American Refining Corporation. The average tray efficiency obtained on the toluene recovery tower was 50%, while the stripper efficiency was 45%.

A McCabe-Thiele diagram, drawn on a phenol-free basis, is used for studying the fractionation in the toluene recovery tower.

This process for toluene purification is licensed by the Shell Development Company.

Description of Commercial Unit

In this section of the paper, the equilibrium relationships obtained in Section I are applied to an analysis of the operation of the toluene recovery plant of the Pan-American Refining Corporation at Texas City, Texas. The unit consists of a tower for separating toluene from non-aromatics and a tower for stripping the toluene from the phenol. These will be hereinafter referred to as the toluene recovery tower and the stripper, respectively. The physical features of the towers are listed in Table I. Figure 1 is a diagrammatic flow sheet of the system. All trays are numbered from the bottom of each tower. The preheated hydrocarbon charge is fed to the nineteenth tray of the toluene recovery tower, while the stripper bottoms, after cooling, are fed to the thirty-ninth tray of the recovery tower. The non-aromatics are taken overhead, and the bottoms, consisting of toluene and phenol (plus sludge), are charged to the stripper where toluene is recovered overhead and the phenol is recirculated. Both towers operate with total condensers and pump back reflux.

A complete test was run on this system on October 7, 1943, from 8 a.m. to 2 p.m. Six hour composite samples were taken at all the points indicated in Table I. All hot samples were taken through a cooler to prevent flashing. The tray samples were taken from the valves on the tower connected into the downspout of the tray whose number was used to designate the sample. These valves were piped to coolers on the various decks. All lines and valves were drained and the sample was allowed to flow for about thirty seconds to be sure that all material in the lines was displaced before a sample was taken. This insured representative samples at all points.

* Pan American Refining Corp., Texas City, Texas.

TABLE I.—DESCRIPTION OF TOWERS TOLUENE-PURIFICATION UNIT

	Toluene Recovery Tower		Stripper
Diameter	7'0"		4'0"
Number of Trays	65		30
Tray Spacing	18"		18"
Type Flow	Double		Single
	center	end	
Down Flow Area (% of tray area)	5.3	6.9	4.9
Riser Area (% of tray area)	11.2	10.3	10.4
Weir Length	133"	116"	38"
Feed Tray (all trays numbered from bottom of tower)			
Hydrocarbon	19		14
Phenol	39		
Temperature Points	Tower Top Reflux Drum Reboiler Outlet Tray 8 14 18 34 38		Tower Top Reflux Drum Reboiler Inlet Reboiler Outlet Tray 3 9 13 22
Pressure Points	Reflux Drum Tower Top Tray 36 Tower Bottom		Reflux Drum Tower Top Tray 14 Tower Bottom
Samples	Hydrocarbon Charge Phenol Charge Overhead Bottoms Tray 61 59 57 55 53 51 49 47 45 43 41 39 37 35 31 27 23 18 15 11 7 3		Charge (Recovery Tower Bottoms) Overhead (Recovery Tower Phenol Charge) Tray 9 13

The flows were obtained from flow recorders which were checked and recalibrated within the previous seventy-two hours. The pressure gauges, temperature recorders, and thermocouples were also checked within this period.

A second test was run on the system on February 16, 1944, using substantially the same procedure. This test was not so complete with regard to sampling and analysis as the test of October 7th. However, sufficient data were obtained to calculate the toluene recovery tower.

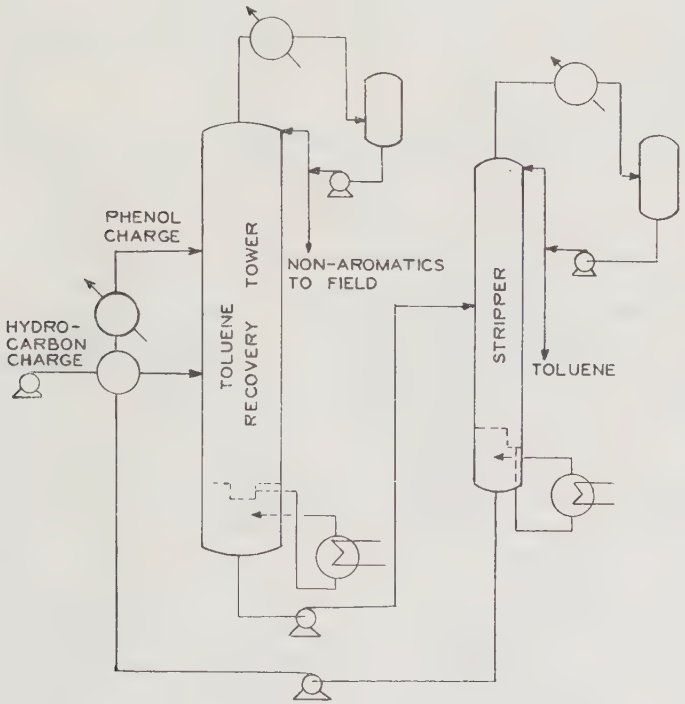


FIG. 1.

The flows, temperature, and pressures were constant throughout each test, and at least twelve hours of constant operation were obtained previous to the start of the tests.

TEST OF OCTOBER 7, 1943

Methods of Analysis

Phenol. Samples from above the phenol feed tray on the toluene recovery tower were analyzed by two methods. Those containing less than 2% phenol were analyzed by the bromide-bromate titration method. Those containing higher amounts of phenol were analyzed by caustic absorption. Samples from below the phenol feed tray contained sludge and therefore

could not be analyzed by caustic absorption. These were distilled in a batch column at 5 to 1 reflux ratio. The first overhead cut was taken up to the phenol plateau at 360° F. This cut was analyzed for phenol by caustic absorption. The distillation was then continued until the temperature rose sharply as the phenol plateau was passed. The total phenol in the sample included this cut plus the phenol in the first cut. The bottoms were counted as sludge. All toluene-recovery-tower samples below tray 39 (including the bottoms) were analyzed in this manner, as well as the tray samples and bottoms sample from the stripper.

Toluene. Samples containing less than 20% toluene (on a phenol-free basis) were analyzed on a Beckman ultra-violet spectrophotometer. Samples containing more than 20% toluene were analyzed by sulphonation with 98% sulphuric acid.

Non-Aromatics. All samples from the toluene recovery tower were dearomatized by successive washings with 98% sulphuric acid. When the refractive index did not change in three tries with an additional washing between each try, the sample was considered to be dearomatized. Distillations were run on the aromatic free charge and overhead and all tray samples down to tray 11. The distillations were run on a Hyper-Cal (W. J. Podbielniak High Temperature Distillation Column) at 20 to 1 reflux ratio. The charge varied from 100 to 300 cc. depending on the amount of aromatic free material available. Temperatures were read at 1% intervals, and each 5% was segregated in a separate cut. In order to insure that the entire sample could be taken overhead it was necessary to add bottoms. When there is too big a gap between the final boiling point of the overhead and the initial of the bottoms, the distillation rate falls off, the tower top temperature drops and the distillation is useless in establishing the analysis. It was shown from preliminary work that these samples had a final boiling point below 260° F. Therefore, bottoms which initialed at 265° F. were fractionated from alkylate. 100 cc. of this material was added to each sample.

Refractive indices were read on the 5% cuts. From these refractive indices, the refractive index of methylcyclohexane, and that of the paraffin in the boiling range of the cut, the per cent methylcyclohexane was established. The true-boiling-point curves were broken into the paraffinic components shown in Table II. For the samples from tray 11 and lower in the toluene recovery tower it was found impractical to isolate sufficient aromatic free material to obtain a true-boiling-point curve. On these (aromatic-free) samples boiling points were run on a micro Cottrell apparatus; refractive indices were also obtained. From these the composition was estimated.

Toluene Recovery Tower. Operating conditions are summarized in Table III. The analyses of the samples in mole per cent are given in Table IV. The hydrocarbon percentages are given on a phenol-free basis, while the phenol and sludge percentages are given on the basis of total liquid. On the basis of the flows, temperatures, and analyses an enthalpy balance was made around the tower, and the reflux duty and reboiler duty were obtained, as shown in Table V. Enthalpy balances around every fifth or sixth tray showed that the reflux ratio did not vary by more than 1% in any section of the tower, so the assumption of constant molal overflow was justified.

TABLE II.—PARAFFINIC COMPONENTS TOLUENE RECOVERY TOWER

Component ° F.	Boiling Range ° F.	Specific Gravity at 60° F.	Molecular Weight
195	IBP-203	.683	100
210	204-215	.694	104
220	216-225	.699	114
230	226-235	.698	114
240	236-243	.720	114
245	244-248	.725	114
255	249-FBP	.710	118

TABLE III.—TEST OF OCTOBER 7, 1943, OPERATING CONDITIONS

Toluene Recovery Tower		Stripper	
Flows, bbl./day		Flows	
Hydrocarbon charge	1828	Charge	5590
Phenol charge	4670	Overhead	920
Overhead	908	Reflux	1048
Bottoms	5590	Bottoms	4670
Reflux	2500		
Temperatures, ° F.		Temperatures	
Hydrocarbon charge	237	Charge	340
Phenol charge	292	Tower top	240
Tower top	224	Reflux drum	189
Reflux drum	177	Reboiler inlet	385
Reboiler outlet	340	Reboiler outlet	400
Tray 8	287	Tray 39	351
14	283	9	326
18	281	13	324
34	279	22	246
38	277		
Pressures, lb./sq.in. gage		Pressures	
Tower top	2.3	Tower top	0.7
Reflux drum	1.0	Reflux drum	0.5
Tower bottom	5.0	Tower bottom	5.5
Tray	3.6	Reflux drum	2.8

TABLE IV.—TEST OF 10-7-43 ANALYSIS OF SAMPLES—TOLUENE RECOVERY TOWER

Composition, Mole %	Charge	Overhead	Tray Number 63	61	59	57	55	53	51	49	47	45	43
195 ° F.	6.4	14.9	6.8	5.3	4.4	4.5	3.9	3.9	3.9	3.5	3.1	3.8	4.1
210	12.8	30.1	20.2	17.6	14.6	14.0	13.8	13.8	11.1	13.2	10.2	9.4	9.3
220	1.8	4.2	4.3	4.7	3.4	3.8	2.9	2.5	2.5	2.5	2.2	3.0	2.0
230	1.3	3.0	5.6	4.4	5.0	5.8	3.9	3.1	2.9	3.4	2.3	7.0	3.5
240	4.1	9.7	16.7	17.1	19.5	18.3	19.0	20.4	18.2	19.3	17.3	16.6	16.9
245	3.8	8.8	20.2	21.6	25.7	27.6	32.9	29.2	33.0	30.5	31.3	27.6	28.4
255	.6	1.5	2.5	5.6	7.0	8.3	8.6	12.1	13.7	14.8	18.2	19.0	22.3
Methylcyclohexane	5.8	13.5	9.9	11.5	9.3	7.4	5.8	7.1	7.6	6.0	8.3	6.7	6.0
Toluene	63.4	14.3	13.8	12.2	11.1	10.3	9.2	7.9	7.1	6.8	7.1	6.9	7.5
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Phenol		.2	.64	.93	1.23	1.46	1.81	2.19	2.49	3.01	3.57	4.24	4.70
Sludge													
Composition, Mole %	41	39	37	35	31	27	23	18	15	11	7	3	Bottoms
195	4.4	2.5	3.0	3.5	2.4	1.6	2.0	1.7	.7				
210	11.5	9.4	10.4	8.7	5.8	5.0	3.8	4.5	1.7				
220	1.6	2.0	1.9	1.5	1.0	1.0	.5	.7	.4				
230	3.2	1.3	2.7	1.6	1.1	.8	.6	.7	.4				
240	16.5	13.5	10.5	6.8	4.6	3.5	2.2	2.1	1.2	.7			
245	26.8	22.5	19.5	16.3	8.9	4.4	3.0	3.4	1.8	1.7	1.0	.4	.1
255	22.4	28.6	22.2	18.7	9.8	4.9	4.8	2.6	2.0	2.6	1.8	1.0	.5
Methylcyclohexane	6.0	6.5	8.5	7.6	6.0	4.8	4.0	3.9	2.5	1.7	1.0	.3	
Toluene	7.6	13.7	21.3	35.3	60.4	74.0	79.1	80.4	89.3	93.3	96.2	98.4	99.4
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Phenol	6.88	53.6	53.5	53.2	53.2	53.2	52.8	43.7	43.8	43.9	44.0	44.3	62.0
Sludge		19.8	19.4	19.2	19.0	19.0	19.5	15.0	15.0	14.8	14.9	15.0	22.6

Hydrocarbon compositions are on a phenol-free basis.

Tray-to-tray calculations for a non-ideal system are similar to ordinary tray-to-tray calculations in ideal systems; however, the ideal equilibrium constants must be corrected for the deviation from Raoult's Law. The activity coefficient, which gives the ratio of the actual to the ideal K, is the measure of this deviation. Since the activity coefficients are correlated with the composition of the liquid phase, any dew-point calculations (as in the rectifying section of a tower) involve an additional trial and error. The liquid composition must be assumed in order to estimate activity coefficients. In general, the variation in activity coefficients with composition is not sharp enough to necessitate more than two trials, so that the calculation is not unduly tedious.

TABLE V.—ENTHALPY BALANCE—TOLUENE RECOVERY TOWER TEST OF 10-7-43

Reflux Duty

	B.t.u./hr.
Lb. Reflux (enthalpy of vapor at 224° F. — enthalpy of Liquid at 176° F.) 26,500(350-184)	= 4,400,000

Heat In

Enthalpy of hydrocarbon charge (as liquid at 237° F.) 21,297 × 222	4,730,000
Enthalpy of phenol charge* (as liquid at 292° F.) 72,090 (261.2)	18,810,000
Reboiler duty (by difference)	8,525,000
	32,065,000

Heat Out

Reflux duty	4,400,000
Overhead (as vapor at 224° F.) 9,610 (350)	3,365,000
Bottoms (as liquid at 340° F.)	
Phenol* 72,090 (290)	20,900,000
Hydrocarbons 11,686 (291)	3,400,000
	32,065,000

All enthalpies based on zero enthalpy for liquid at —200° F.

INTERNAL REFLUX RATIOS

Toluene Recovery Tower

Section

Trays 40-65	$L/V = .765$	
20-39	$L/V = .704$	(phenol-free basis)
1-19	$L'/V' = 1.32$	(phenol-free basis)

* Includes sludge.

On the basis of the charge, overhead, and bottoms analyses, tray-to-tray calculations were made. Table VI illustrates the calculation for a typical tray above the phenol feed tray.

TABLE VI.—TRAY CALCULATION—TOLUENE RECOVERY TOWER—ABOVE PHENOL FEED TRAY TEST OF 10-7-43

Component° F.	L_n	D	V_{n+1}	$P_{240°}$	γ	α	$\frac{V_{n+1}}{\alpha}$	L_{n+1}
195 Cut	18.70	13.70	32.40	27.5	1.00	1.335	24.2	16.2
210	60.70	27.80	88.50	22.8	1.00	1.108	80.0	53.5
220	12.19	3.90	16.09	20.0	1.00	.97	16.6	11.1
230	12.25	2.80	15.05	17.2	1.00	.835	18.1	12.1
240	54.50	9.00	63.50	14.7	1.00	.735	86.4	57.7
245	63.10	8.20	71.30	13.7	1.00	.665	107.1	71.8
255	16.90	1.40	18.30	11.8	1.00	.573	31.9	21.3
MCH	28.40	12.50	40.90	22.0	1.00	1.07	38.2	25.6
Toluene	37.20	13.30	50.50	17.2	1.20	1.00	50.5	33.8
Phenol	3.10	.20	3.30	1.59	7.00	.54	6.1	4.1
	307.04	92.80	399.84				459.1	307.2

$$K_{\text{toluene}} = \sum \frac{1}{\alpha} = 1.16 = \frac{P_{\text{toluene}} \times \gamma}{17.7} = 1.165$$

L_n, L_{n+1} = moles liquid overflowing from tray
V_{n+1} = moles vapor leaving tray
D = moles net overhead
$P_{240°}$ = vapor pressure at 240° F.
γ = activity coefficient
α = relative volatility to toluene

Tower pressure above phenol feed tray = 17.7 lb./sq.in.abs.

Below the phenol feed tray the phenol concentration in the vapor can be established from the equation for constant composition from tray to tray:

$$v = \frac{b}{\frac{L}{KV} - 1}$$

where

b = moles phenol in bottoms
v = moles phenol in vapor
K = equilibrium constant = $\frac{P_1}{P} \times \gamma_1$
P_1 = phenol vapor pressure
γ_1 = activity coefficient of phenol
P = total pressure
L = total liquid overflow from tray
V = total vapor leaving tray

At the phenol concentration on the trays, 40% to 70%, the variations in the phenol activity coefficient with changing hydrocarbon composition are not significant. Since the change in temperature from tray to tray is small except at the very bottom, the K for phenol will remain constant

xcept at the very bottom of the tower. The per cent phenol on the trays vill change only where the values of L and V change at the hydrocarbon eed tray. The phenol concentration on the trays can thus be established rom a single calculation above the hydrocarbon feed tray and one calculaion below this tray, and phenol need be carried as a component in the ray-to-tray calculations only for a few trays at the bottom until it reaches ts minimum concentration. Tables VII and VIII present typical tray calculations on a phenol-free basis, from above and below the hydrocarbon eed tray.

TABLE VII.—TRAY CALCULATION—TOLUENE RECOVERY TOWER RECTIFYING SECTION BELOW PHENOL FEED TRAY PHENOL FREE BASIS, TEST OF 10-7-43

Component ° F.	L_n	D	V_{n+1}	$P_{275°}$	γ	α	$\frac{V_{n+1}}{\alpha}$	L_{n+1}
95	6.7	13.7	20.4	47.8	2.90	3.7	5.5	6.2
10	19.8	27.8	47.6	38.2	2.90	2.96	16.1	18.0
20	3.6	3.9	7.5	33.0	2.90	2.56	2.9	3.3
30	3.8	2.8	6.6	28.9	2.90	2.23	3.0	3.4
40	20.5	9.0	29.5	24.9	2.90	1.93	15.3	17.1
45	34.9	8.2	43.1	22.9	2.90	1.78	24.2	27.1
55	41.1	1.4	42.5	19.2	2.90	1.49	28.5	32.0
MCH	13.8	12.5	26.3	37.5	2.20	2.20	12.0	13.5
Toluene	76.0	13.3	89.3	28.9	1.29	1.00	89.3	100.1
	220.2	92.6	312.8				196.8	220.7

L_n, L_{n+1} = moles hydrocarbon liquid overflowing from tray
V_{n+1} = moles hydrocarbon vapor leaving tray
D = moles hydrocarbon overhead
$P_{275°}$ = vapor pressure at 275°
γ = activity coefficient
α = relative volatility to toluene

71.6% phenol on trays (sludge-free basis)
38 moles/hr. phenol in vapor
545 moles/hr. phenol in liquid

The sludge was assumed to have zero vapor pressure and was carried nerely as an inert material in the enthalpy balances. The vapor pressures of other components were read from Figure 2.

The following overall tray efficiencies were calculated:

Section	Actual Trays	Theoretical Trays	Per Cent Tray Efficiency
1-19	19	10.0	52.7
20-39	20	9.7	48.5
40-65	26	13.0	50.0

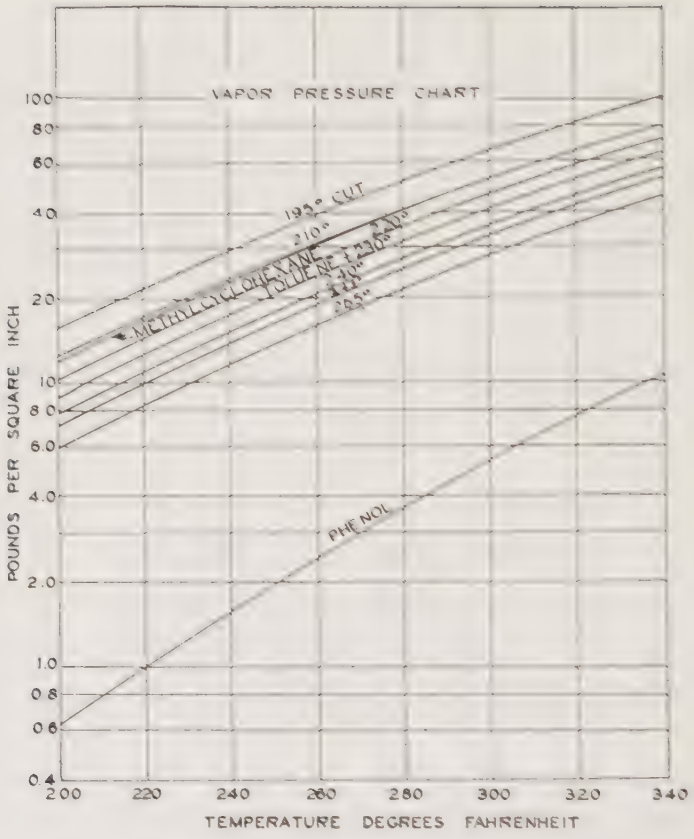


FIG. 2.

TABLE VIII.—TRAY CALCULATION—TOLUENE RECOVERY TOWER STRIPPING SECTION—PHENOL FREE BASIS, TEST OF 10-7-43

Component ° F.	V_m	B	L_{m+1}	$P_{280°}$	γ	α	$L_{m+1}\alpha$	V_{m+1}
195	2.7		2.7	51.1	2.60	3.68	9.95	6.45
210	12.5		12.5	40.8	2.60	2.94	36.80	23.85
220	2.7		2.7	35.0	2.60	2.55	6.90	4.47
230	2.7		2.7	30.9	2.60	2.20	5.95	3.86
240	9.7	.1	9.8	26.5	2.60	1.90	18.62	12.10
245	15.0	.2	15.2	24.6	2.60	1.76	26.80	17.40
255	13.4	.4	13.8	21.0	2.60	1.46	20.20	13.10
MCH	12.1	.1	12.2	39.0	1.93	2.09	25.50	16.54
Toluene	308.0	126.0	434.0	30.9	1.17	1.00	434.00	282.00
	378.8		505.6				584.72	379.77

L_{m+1} = moles hydrocarbon liquid overflowing from tray
V_m, V_{m+1} = moles hydrocarbon vapor leaving tray
B = moles hydrocarbon bottoms
$P_{280°}$ = vapor pressure at 280°
γ = activity coefficient
α = relative volatility to toluene

52.6% phenol on trays (sludge-free basis)
52 moles phenol in vapor
560 moles phenol in liquid

[illegible]

[illegible]

[illegible]

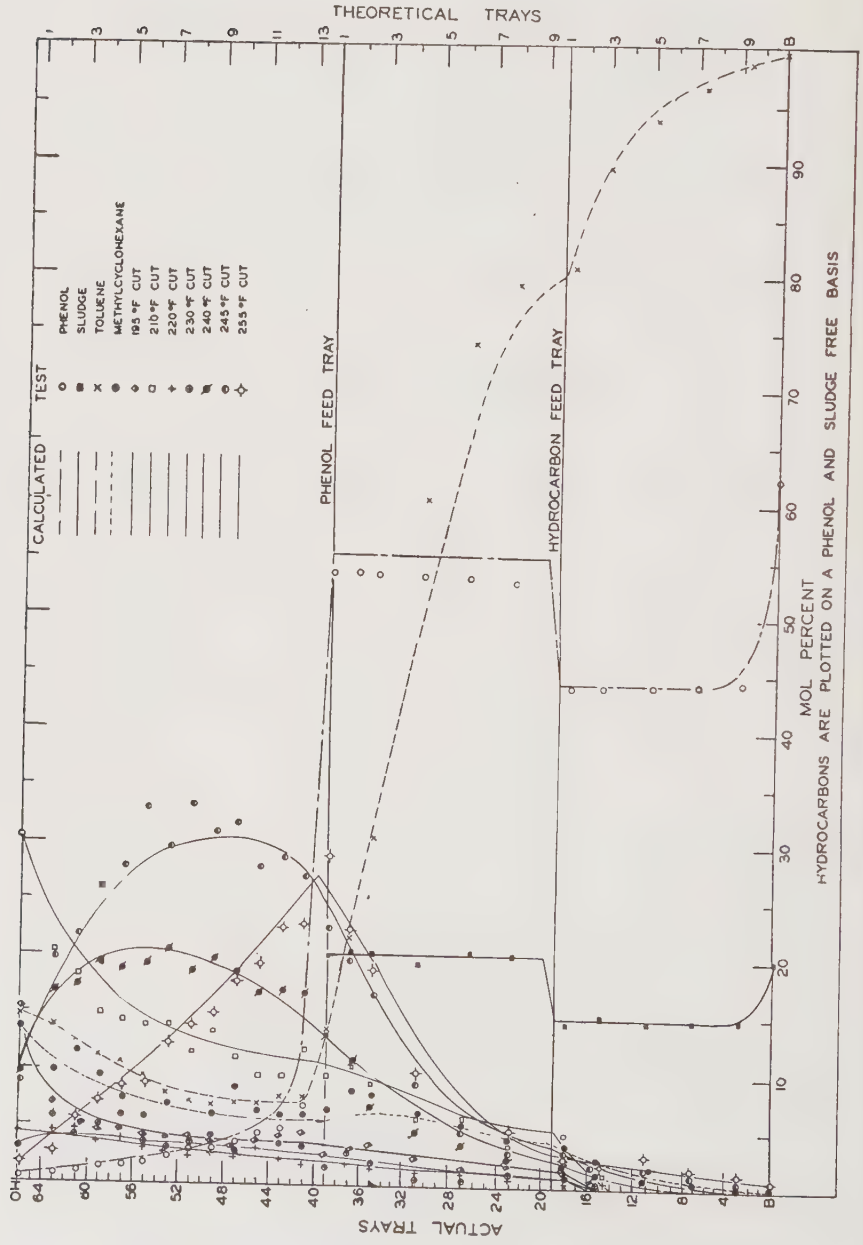


Fig. 3. Tolusana Recovery Tower Test 6 (10-7-42)

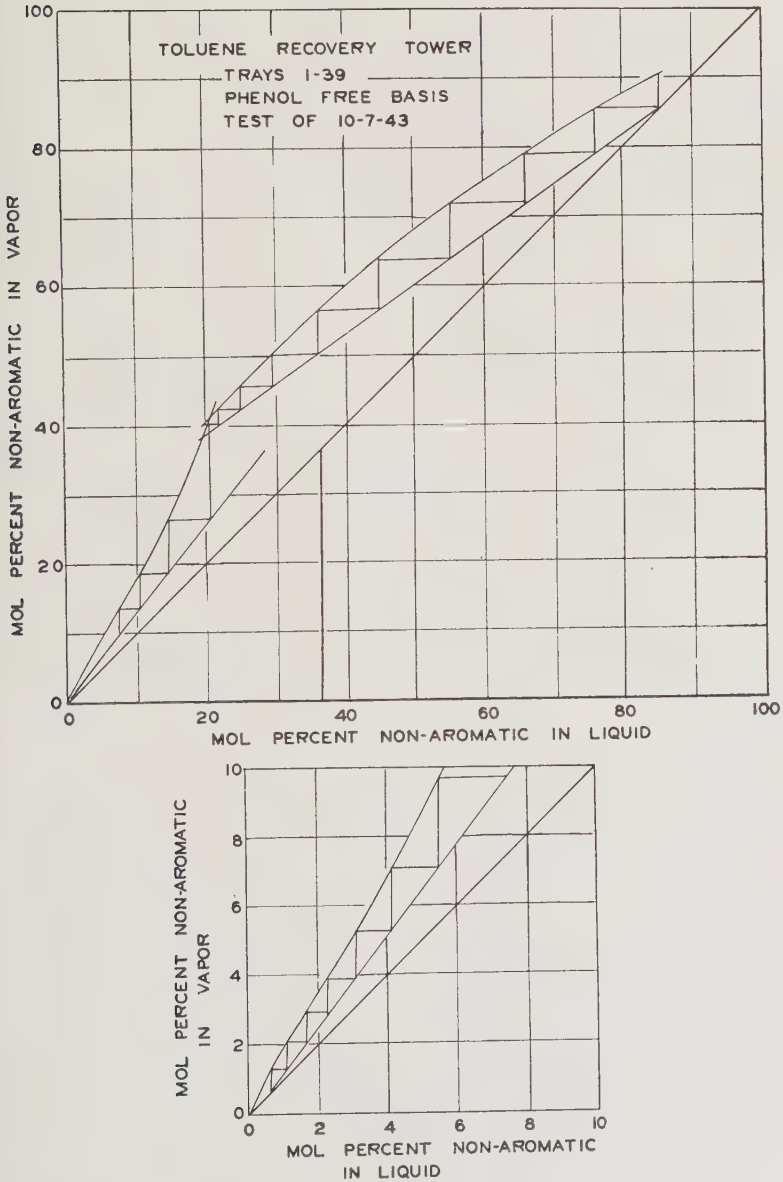

TOLUENE RECOVERY TOWER
TRAYS 1-39
PHENOL FREE BASIS
TEST OF 10-7-43
MOL PERCENT NON-AROMATIC IN VAPOR
MOL PERCENT NON-AROMATIC IN LIQUID
0
20
40
60
80
100
MOL PERCENT NON-AROMATIC IN VAPOR
MOL PERCENT NON-AROMATIC IN LIQUID
0
2
4
6
8
10

FIG. 4.

TABLE X.—ENTHALPY BALANCE ON STRIPPER TEST OF 10-7-43

	B.t.u./hr.
Reflux Duty	
Pounds reflux (enthalpy as vapor at 240° F.—enthalpy as liquid at 189° F.) 13,300 (380-200)	2,890,000
Heat In	
Hydrocarbon charge (as liquid at 340° F.) 11,686 (291)	3,400,000
Phenol charge * (as liquid at 340° F.) 72,090 (290)	20,900,000
Reboiler duty (by difference)	6,119,000
	30,419,000
Heat Out	
Reflux duty	2,890,000
Overhead (as vapor at 240° F.) 11,200 (380)	4,259,000
Bottoms * (as liquid at 400° F.) 72,576 (321)	23,270,000
	30,419,000

All enthalpies based on zero enthalpy for liquid at —200° F.

* Includes sludge.

TABLE XI.—OPERATING LINES IN THE STRIPPER TEST OF OCTOBER 7, 1943

Rectifying Section		Stripping Section	
Temp., ° F.	$\frac{L}{V}$	Temp., ° F.	$\frac{L'}{V'}$
240	.555	390	2.73
260	.54	375	2.94
270	.525	360	3.12
280	.505	345	3.36
290	.488	339	3.49
300	.472	335	3.59
310	.456	331	3.67
320	.441	328	3.85
325	.437		
330	.428		

On sludge-free basis.

TABLE XII.—ANALYTICAL DATA—STRIPPER TEST OF OCTOBER 7, 1943

Sample	Mole % Toluene	Mole % Phenol	Mole % Sludge
Charge	15.4	62.0	22.6
Overhead	99.942	.058	
Bottoms	.89	72.70	26.41
Tray 13	16.8	62.9	20.3
Tray 9	14.8	64.4	20.8

plotted as a pseudo binary system with toluene and non-aromatics as the two components. As suggested by J. E. Kasch [2] the equilibrium curve and operating line are plotted on a phenol-free basis. The sharp change in the equilibrium curve at the hydrocarbon feed tray is due to the drop in per cent phenol in the liquid on the trays below the hydrocarbon feed. It can be seen that two extra steps (theoretical trays) in the stripping section would effect a much larger change in toluene concentration than is accomplished by the bottom theoretical trays in the rectifying section.

It is interesting to note the sharp maximum in the profile of the 255° F. paraffin component which occurs at the phenol feed tray. Above this tray the 255° component is one of the least volatile components and increases in concentration coming down the tower. Below the thirty-ninth tray the phenol so increases the paraffin activity coefficient that the equilibrium curve for the 255° F. component is immediately transferred above the operating line. This maximum is qualitatively similar to a maximum which may occur in any fractionation where the equilibrium curve and operating line cross, but it is much sharper due to the sudden change in volatility of the paraffinic component.

The methylcyclohexane profile shows a double curvature. Above the phenol feed tray the methylcyclohexane decreases in composition coming down the tower. Since phenol does not affect methylcyclohexane as much as paraffins, it becomes a less volatile component at the phenol feed tray. However, as the toluene (which is less affected than methylcyclohexane by phenol) builds up, the methylcyclohexane equilibrium curve and operating line recross and the methylcyclohexane is rectified out of the liquid.

The phenol activity coefficient in the section of the toluene recovery tower above the phenol feed tray was calculated using Figure 15 (Section I) and the assumptions listed in Section I. The results of the tray-to-tray calculations are plotted in Figure 5 as a binary phenol-hydrocarbon system.

Vapor-liquid equilibria were then run on the tray samples from the upper section of the tower. It was realized that the equilibria obtained were not strictly comparable to the equilibria occurring in the tower, as the composition of the hydrocarbon in the pot of the Othmer still was not the same as the hydrocarbon on the trays. However, since only about 20 cc. out of a charge of over 200 cc. were taken overhead on the Othmer still, the error involved should not impare the usefulness of the data. The equilibrium data obtained are plotted in Figure 5. The agreement between the experimental points and the calculated equilibrium curve is sufficiently close to show that the method used for calculating the phenol activity coefficient in dilute phenol-hydrocarbon solutions is satisfactory.

The Stripper. Essentially the only components in the stripper are toluene, phenol, and sludge. Since sludge could be considered to have zero vapor pressure and no effect on the equilibrium between toluene and phenol, the tower could be calculated as a binary system using a McCabe-Thiele diagram. Both the equilibrium curve and operating lines were calculated on a sludge-free basis. In this case the assumption of constant molal overflow was not valid, so it was necessary to plot curved operating lines based on the heat balance shown in Table X. Table XI shows the slope of the operating lines as a function of tower temperature. The analyses of the various streams including tray samples are shown in Table XII.

The tower was calculated by stepping off trays graphically on an $x - y$ diagram. Figure 6 illustrates the procedure. A tray efficiency of 60.70% was obtained in the rectifying section, while the stripping section efficiency was 37.8%. As is shown by the temperatures and tray analyses from trays 9 and 13, there is a considerable zone of substantially constant composition immediately below the feed tray. The difficulty of getting an accurate value for the number of trays necessary to fractionate through a

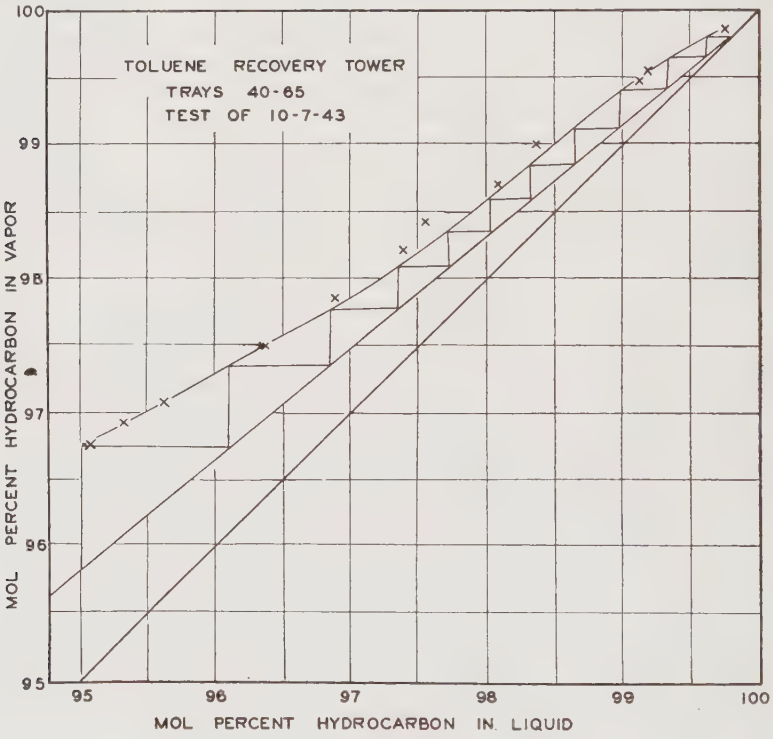


FIG. 5.

zone of constant composition may have some effect on the tray efficiency in the stripping section, though the difference in viscosity would indicate a difference in tray efficiency of the order of magnitude of that which was obtained.

TEST OF FEBRUARY 16, 1944

Toluene Recovery Tower

On February 16, 1944, another test was run on the toluene recovery tower. The operating conditions are shown in Table XIII. Not as many samples were taken and the analytical data were not as complete. The samples taken and their analyses are listed in Table XIV.

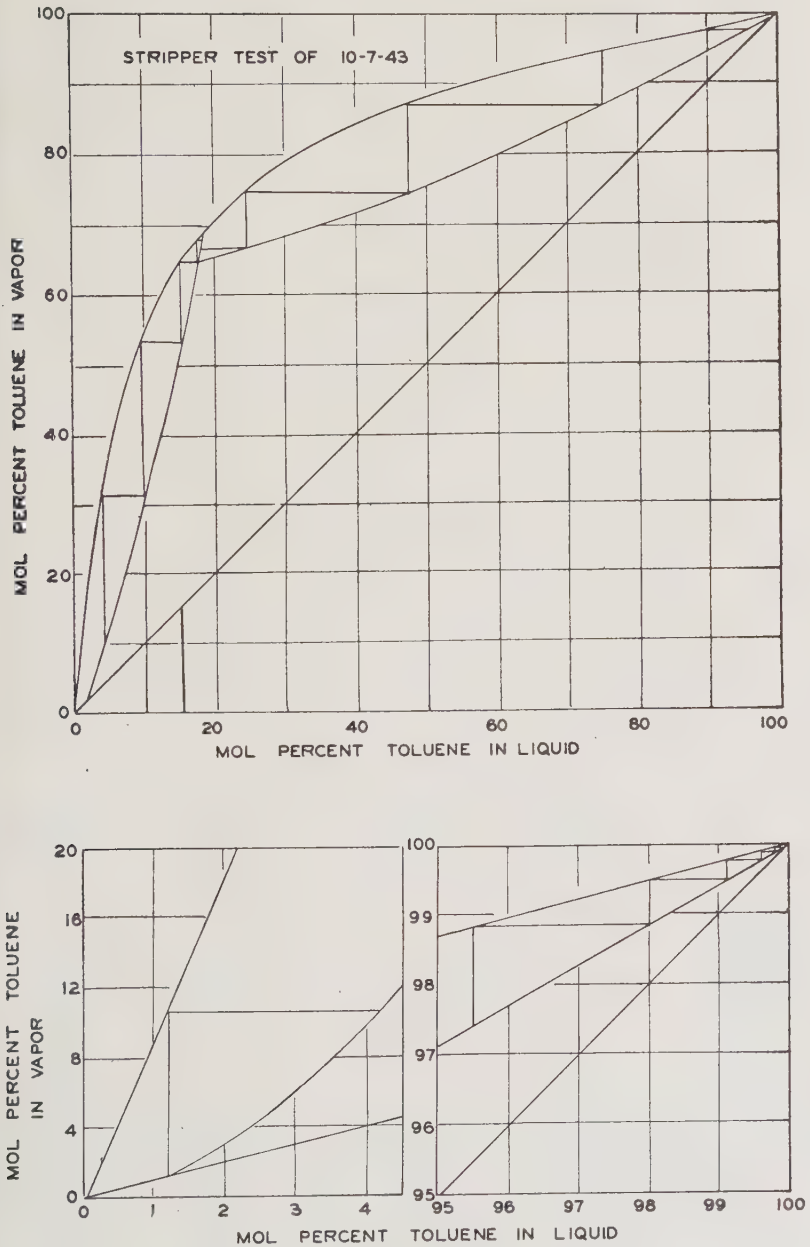

STRIPPER TEST OF 10-7-43
MOL PERCENT TOLUENE IN VAPOR
MOL PERCENT TOLUENE IN LIQUID
0
20
40
60
80
100
MOL PERCENT TOLUENE IN VAPOR
MOL PERCENT TOLUENE IN LIQUID
0
4
8
12
16
20
95
96
97
98
99
100

FIG. 6.

TABLE XIII.—OPERATING CONDITIONS TEST OF FEBRUARY 16, 1944

Flows, bbl./day	
Hydrocarbon charge	1935
Phenol charge	4540
Overhead	1050
Bottoms	5425
Reflux	2500
Temperatures, ° F.	
Hydrocarbon charge	232
Phenol charge	292
Tower top	224
Reflux drum	200
Reboiler outlet	340
Tray 8	284
14	282
18	280
34	277
38	274
Pressures, lb./sq.in. gage	
Tower top	2.6
Reflux drum	1.0
Tower bottom	5.0
Tray 35	3.8

INTERNAL REFLUX RATIO

Trays	
40-65	$L/V = .72$
20-39	$L/V = .656$
1-19	$L'/V' = 1.36$

	B.t.u./hr.
Reboiler duty	8,250,000
Reflux duty	4,065,000

TABLE XIV.—ANALYTICAL DATA TEST OF FEBRUARY 16, 1944

Sample	Mole % Toluene in the Hydrocarbon	Mole % Phenol in Total Sample	Mole % Sludge in Total Sample	Cottrell Boiling Point
Hydrocarbon Charge *	58.0			
Phenol Charge		71.6	28.4	
Overhead	9.06	.35		216.0†
Bottoms	98.4	59.0	23.0	
Tray 61	8.63	1.08		227.0†
55	6.46	1.98		232.0†
49	5.37	2.96		235.0†
43	5.64	4.1		238.0†
39	11.0			238.5‡
35	26.0	55.4	22.1	233.0‡
31	47.6			231.0‡
27	62.8	55.1	23.0	229.0‡
23	69.4			228.0‡
18	70.8			228.6‡
15	79.1	43.7	17.0	236.0‡
11	86.7			240.0‡
7	92.62	45.0	16.8	243.0‡
3	96.13			245.0‡

* Eight mole % methylcyclohexane on charge.
† Taken on phenol-free material.
‡ Taken on aromatic-free material.

It should be noted that the charge has a lower toluene concentration than in the test of October 7, 1943. The internal reflux is lower due to the higher reflux drum temperature. The phenol and sludge concentrations are essentially the same as before. The major operating change is the change in cut point, giving 1.6 mole % non-aromatics in the toluene product, as compared with 0.6 mole % in the earlier test. This results in lower toluene concentrations throughout the tower. A consequence of the lower toluene concentrations above the phenol feed tray is the increased phenol loss (from 0.2% to 0.35%) in the overhead.

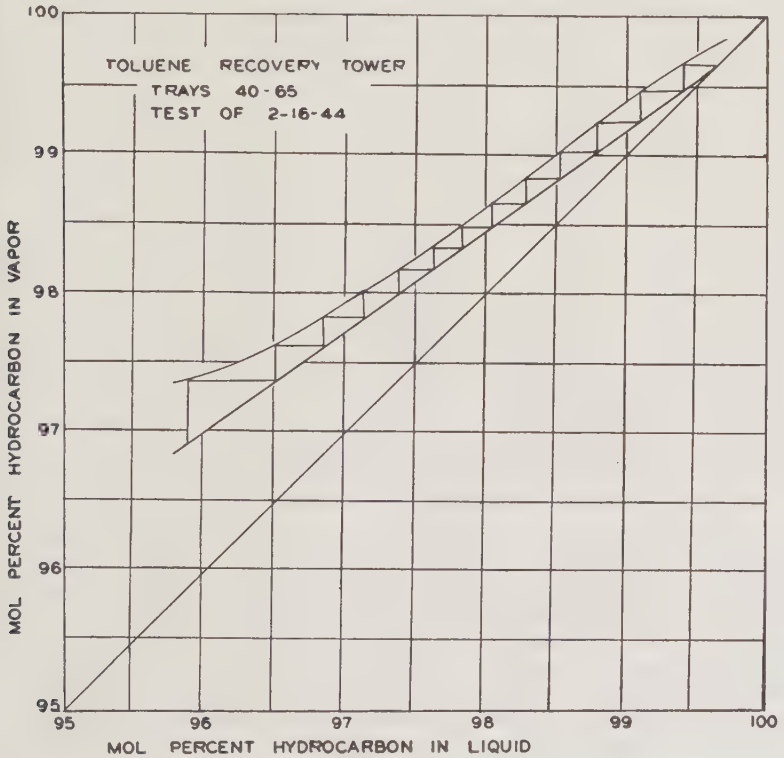


FIG. 7.

The number of theoretical trays were calculated using a pseudo McCabe-Thiele diagram such as was plotted from the tray to tray calculation on the test of October 7, 1943. The equilibrium curve for the section above the phenol feed tray was plotted by calculating the relative volatilities of phenol and hydrocarbon. The tray temperatures were estimated from the operating data. The ideal relative volatility was taken as the relative vapor pressure, at the tray temperature, of phenol, and of a hydrocarbon boiling at the Cottrell boiling point of the tray sample hydrocarbon. The activity coefficient of phenol was calculated by the method used for the test of October 7th. Table XV illustrates this method. The reflux ratios

were established by heat balances. The theoretical trays were then stepped off as shown in Figure 7. A tray efficiency of 56.9% was calculated for the section from the forty-third through the sixty-fifth tray.

TABLE XV.—EQUILIBRIUM CALCULATIONS—TOLUENE RECOVERY TOWER ABOVE PHENOL FEED TRAY—TEST OF FEBRUARY 16, 1944

Tray No.	Boiling Point of the Hydrocarbons ° F.	Tray Temp., ° F.	Mole % Phenol	Mole % Toluene in Hydrocarbon	Vapor Pressure of Phenol	Vapor Pressure of Hydrocarbon	α Ideal
Overhead	216	224	0.35	9.06	1.10	17	15.45
61	227	230	1.08	8.63	1.22	16	13.1
55	232	233	1.98	6.46	1.33	15	11.3
49	235	236	2.96	5.37	1.44	15	10.4
43	239	245	4.10	5.64	1.78	16.4	9.2

	γ_1	$\gamma_1 x_1$	γ_2	$\gamma_2 x_2$	γ	α
Overhead	10.9	9.9	2.69	.20	10.1	1.55
61	9.8	8.9	2.66	.17	9.07	1.49
55	8.5	8.0	2.63	.15	8.15	1.43
49	7.6	7.2	2.60	.14	7.34	1.46
43	6.03	5.68	2.53	.13	5.81	1.58

γ_1 = activity coefficient of phenol in a paraffin solution of this phenol concentration
γ_2 = activity coefficient of phenol in a toluene solution of this phenol concentration
x_1 = mole fraction non-aromatic in the hydrocarbon
x_2 = mole fraction toluene in the hydrocarbon
α = relative volatility of hydrocarbon to phenol

The equilibrium curve in the lower part of the tower was calculated from the relative volatilities of toluene and non-aromatic in the presence of phenol. The method is illustrated in Table XVI and Figure 8. There were nine theoretical trays in the rectifying section (to and including the phenol feed tray) giving a tray efficiency of 45%. There were 9.6 theoretical trays in the stripping section indicating an efficiency of 50.6%.

It may be noted that, although the cut point was changed, there was still a zone of constant composition above the hydrocarbon feed tray, making the calculated efficiency in the section from tray 20 to tray 39 somewhat unreliable.

The small variation in the ideal volatility of the non-aromatic below the phenol feed tray suggests that where the charge is as narrow boiling as in this case, the phenol-free McCabe-Thiele diagram may be satisfactory for preliminary tower design.

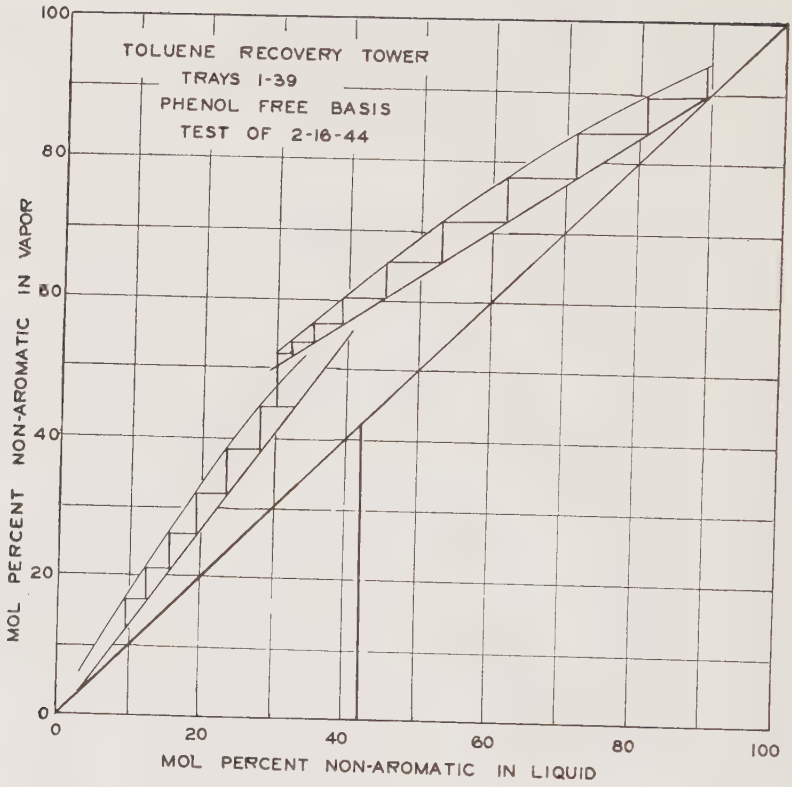
COMPARISON BETWEEN THE TEST OF OCTOBER 7, 1943, AND FEBRUARY 16, 1944

The only major differences between the test conditions were the changes in cut point, a slight decrease in internal reflux ratio, and de-

TABLE XVI.—EQILIBRIUM CALCULATIONS—TOLUENE RECOVERY TOWER BELOW PHENOL FEED TRAY—TEST OF FEBRUARY 16, 1944

Tray No.	Non-Aromatic Boiling Point, ° F.	Tray Temp., ° F.	Non-Aromatic Vapor Pressure *psig*	Toluene Vapor Pressure	Ideal α ‡	Per Cent Phenol *	Per Cent Toluene †	$\frac{\gamma \text{ Paraffin}}{\gamma \text{ Toluene}}$	α‡
39	238.5	275	25.7	28.5	.902	71.4	11.0	2.00	1.8
35	233	275	28	28.5	.982	"	26.0	2.16	2.12
31	231	276	29	29	1.0	"	47.6	2.28	2.28
27	229	277	30.6	29.8	1.028	"	62.8	2.4	2.465
23	228	278	31.0	30.1	1.03	"	69.4	2.43	2.5
18	228.6	278	31.5	30.6	1.03	52.5	70.8	2.05	2.115
15	236	281	28.5	31.0	.92	"	79.1	2.15	1.98
11	240	282	27.5	31.5	.872	"	86.7	2.27	1.98
7	243	285	27.5	32.9	.838	60	92.62	2.31	1.935
3	245	290	28.6	35.0	.817	80	96.13	2.45	2.0
Bottoms	250	340	49.0	64.5	.76		98.4	3.0	2.8

* On sludge-free basis.
† As per cent of total hydrocarbon.
‡ α = relative volatility of non-aromatic to toluene.


TOLUENE RECOVERY TOWER
TRAYS 1-39
PHENOL FREE BASIS
TEST OF 2-16-44
MOL PERCENT NON-AROMATIC IN VAPOR
MOL PERCENT NON-AROMATIC IN LIQUID
0
20
40
60
80
100

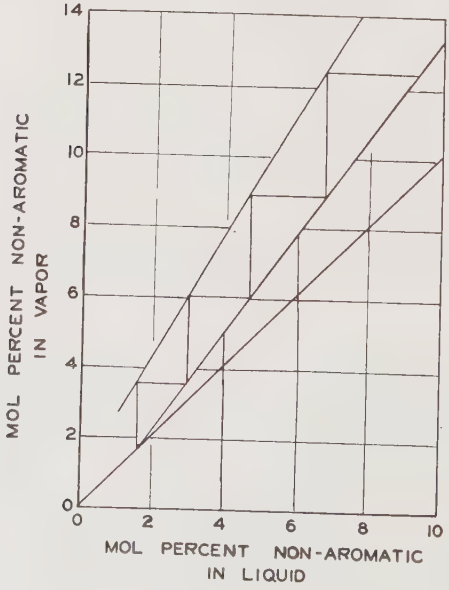

MOL PERCENT NON-AROMATIC IN VAPOR
MOL PERCENT NON-AROMATIC IN LIQUID
0
2
4
6
8
10
12
14

FIG. 8.

creased toluene in the charge. The two tests give a substantial check on tray efficiency and permit the use of 50% efficiency over at least a limited range of operating conditions. It is interesting to note that the correlation of Drickamer and Bradford [1] predicts an efficiency of 60% above the phenol feed tray and 40% below the feed tray.

Conclusions

The experimental data and correlations of Section I form an adequate basis for study of the operation of a commercial unit for toluene purification from petroleum.

The two tests indicate that the overall efficiency of the extractive distillation tower is 50%, while the efficiency of the stripper is 60% in the rectifying section and 38% in the stripping section.

Because of the narrow boiling range of the hydrocarbon charge and the low volatility of the phenol, the hydrocarbon reflux and per cent phenol remain substantially constant in either section of the extractive distillation tower below the phenol feed, permitting calculations in these sections to be made on a phenol-free basis.

Acknowledgment

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2. Kasch, J. E., "Ph.D. Dissertation," University of Texas, 1942.